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Development of Analytical Test Procedures for Organic Pollutants in Wastewater - Application to Pesticides

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DEVELOPMENT OF ANALYTICAL TEST PROCEDURES FOR ORGANIC POLLUTANTS IN WASTEWATER - APPLICATION TO PESTICIDES

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16. ABSTRACT

The Environmental Protection Agency's Environmental Monitoring and Support Laboratory at Cincinnati has been engaged in the development of test procedures for a multitude of organics in water. Midwest Research Institute was contracted to perform in a development program directed toward a group of 58 pesticides. The objective was to develop procedures that were as similar to each other as possible and were sensitive to 1 µg/liter. By using a standard method, at least as a starting point, and making adjustment as necessary, the number of unique procedures was kept to a minimum.

The experimental approach was to test each pesticide against the standard method, e.g., methylene chloride extraction--Kuderna-Danish evaporation--Florisil cleanup--gas chromatographic determination. Problem areas such as poor recovery, inadequate cleanup, etc., were identified and modifications to circumvent these problems were devised. One major deviation was the use of HPLC for several classes of pesticides.

The general classes or individual pesticides studies (and the number of compounds in the classes) were: organochlorine (6); organonitrogen (7); organophosphorus (19); triazines (9); carbamates and ureas (7); carbendazin and benomyl; cyanazine; carbofuran; 4,4'-methylene-bis(2-chloroaniline); dinoseb; tokuthion; piperalin; piperonyl butoxide; and aldicarb.

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Abstract (concluded):

Generally speaking, recoveries for clean water extraction, 7-day stability, and spiked wastewater were good. The greatest deviation from a single method and the major source of reduced recovery was in the area of cleanup.

The sensitivity goal of the basic protocol (1 µg/liter detection limit) was achieved for 80% of the studied pesticides.

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FOREWORD

The Environmental Protection Agency is charged with improving the condition of the environment for the benefit of people and the natural world which surrounds them. Several laws have been enacted which focus the attention of the Agency on specific environmental concerns and initiate action for their solution. The Clean Water Act of 1977 concentrates on ensuring the high quality of the nation's natural waterways.

In support of this effort the Environmental Monitoring and Support Laboratory-Cincinnati conducts research on laboratory procedures to measure the presence and concentration of chemical pollutants in water. Of particular interest are monitoring methods for toxic organic compounds in wastewater which is discharged from manufacturing plants.

This report describes the development of methods for certain selected pesticides in aqueous samples, particularly in manufacturing wastewater. These methods use common gas chromatography and high pressure liquid chromatography detection following common wet laboratory preparation techniques.

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ABSTRACT

The Environmental Protection Agency's Environmental Monitoring and Support Laboratory at Cincinnati has been engaged in the development of test procedures for a multitude of organics in water. Midwest Research Institute was contracted to perform a development program directed toward a group of 58 pesticides. The objective was to develop procedures that were as similar to each other as possible and were sensitive to 1 µg/liter By using a standard method, at least as a starting point, and making adjustment as necessary, the number of unique procedures was kept to a minimum.

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The general classes or individual pesticides studied (and the number of compounds in the classes) were: organochlorine (6); organonitrogen (7); organophosphorus (19); triazines (9); carbamates and ureas (7); carbendazin and benomyl; cyanazine; carbofuran; 4,4'-methylene-bis(2-chloroaniline); dinoseb; tokuthion; piperalin; piperonyl butoxide; and aldicarb.

Generally speaking, recoveries for clean water extraction, 7-day stability, and spiked wastewater were good. The greatest deviation from a single method and the major source of reduced recovery was in the area of cleanup.

The sensitivity goal of the basic protocol (1 µg/liter detection limit) was achieved for 80% of the studied pesticides.

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SECTION 1

INTRODUCTION

Pursuant to Section 304(h) of the Clean Water Act, as amended in 1977, the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati has been assigned the responsibility for providing test procedures for the measurement of organic pollutants in wastewaters. These procedures are designed for use in monitoring direct discharges from industrial and publically owned treatment works (POTW) sources under the National Pollutant Discharge Elimination System (NPDES) permit system and discharges into a POTW system under pretreatment.

On December 3, 1977, a series of 14 new test procedures were proposed in the Federal Register, for the quantitative measurement of specific organic materials commonly referred to as the "priority pollutants."[1] These 14 methods were developed through in-house and contracted research.

In this study a new group of toxic compounds was addressed. Fifty-eight pesticidal compounds of high interest were selected for method development. As with the priority pollutants some analytical information was available in the literature, but in most cases previous methodology was neither sensitive nor selective enough. The project set guidelines of 1 μg/liter minimum detection level and modern chromatographic separation quality with specific detection.

Another concern also shaped the approach to this project. The Environmental Protection Agency is interested in placing the minimum cost burden on users of these methods while maintaining high quality procedures. To reduce costs, everyday analytical procedures were applied where possible, and costly state-of-the-art techniques were avoided. A "multiresidue" method approach was also followed, wherein several compounds of a given chemical class may be analyzed in a certain sample by one run of the procedure. Extending this idea further, commonality of steps of separate multiresidue procedures can decrease cost by reducing the number of procedural repetitions. For example, incorporation of liquid extraction with methylene chloride followed by Kuderna-Danish extract concentration in as many procedures as possible allows the user to handle a sample just once for analysis of several compound classes covered by different multiresidue procedures. Separate class-selective determination procedures can then be performed.

In concert with the multiresidue method approach, the pesticides were grouped according to chemical and analytical characteristics. Groupings (see Table 1, p. 8) were not always the same after the work was concluded because of what was learned.

This study investigated chromatography, liquid extraction, cleanup, and application to relevant wastewater for each compound. Figure 1 is a flow diagram of the protocol used during the study. A brief investigation of analyte stability in aqueous medium was also performed.

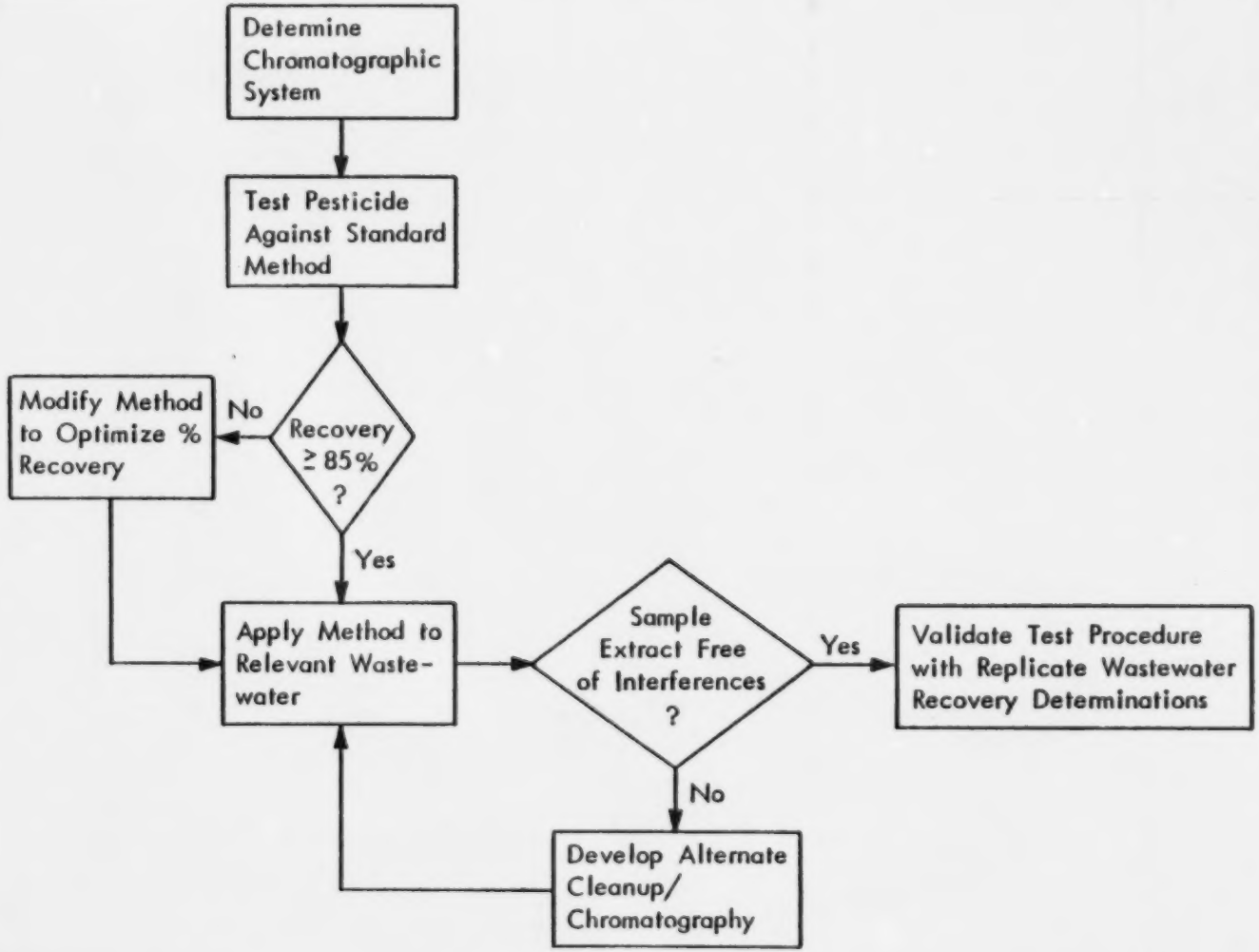


Figure 1. Flow diagram of protocol for development of test procedure.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

This group of 58 pesticides performed well under methylene chloride extraction, absorbent column cleanup, gas chromatography (GC), or high pressure liquid chromatography (HPLC). About 60% of the pesticides could be recovered from activated Florisil using standardized diethyl ether/petroleum ether elution mixture. Less active sorbents and more polar elution solvents were required to obtain satisfactory recovery values. As would be expected, samples from sites with multiproduct integrated waste streams posed both detection and interference difficulties. The methods were most successfully applied to final effluents and to untreated waste which was segregated by the production process.

The study of the applicability of these methods to manufacturing wastewater samples has suggested some areas for improvements or future work. Storage stability studies indicated that even in the benign clean water matrix some pesticides were seriously degraded. Further effort should be directed toward investigation of matrix effects on the integrity of the analyte. This work should also include the development of preservation systems or conditions which allow minimal change to be effected in the overall character of such complex mixtures as waste streams. Alternate methods for extract cleanup including liquid-liquid partitioning or the use of HPLC sorbents should be evaluated for compound classes such as organophosphorus pesticides where recoveries from Florisil are generally poor. Ultimately, there will be a need to assess the environmental impact of the by-products of waste treatment processes. Consequently, analytical methods will be needed both to identify and quantify these decomposition or metabolic products.

SECTION 3

MATERIALS

APPARATUS

Gas chromatography studies were performed using a Varian Model 3700 equipped with electron capture, nitrogen-specific thermionic, and phosphorus-specific flame photometric detectors. Columns were 2-mm ID glass of 1.8 or 1.0 m length. High pressure liquid chromatography studies were performed using a Waters Associates Model 6000A pump, 600 solvent programmer, and 440 detector. The analytical column was 4 mm ID x 30 cm packed with μBondapak C_{18}, 10-μm particle size, from Waters Associates. The guard column was 4 mm x 7 cm packed with CO:PELL ODS from Whatman Company.

Kuderna-Danish apparatus had a volume of 50 ml. Cleanup columes were 20-mm ID x 300-mm pyrex with a coarse fritted disc at bottom and a Teflon stopcock. Solvent drying columns were 19-mm ID x 600-cm (nominal) glass.

REAGENTS

All solvents used were "Distilled-In-Glass" from Burdick and Jackson Company. Anhydrous sodium sulfate was from Supelco Company. Florisil and alumina from Supelco Company were activated for at least 16 hr at 130°C in an open tray prior to use. Florisil was deactivated by adding a measured volume of distilled water to a portion of activated Florisil, followed by agitation for 4 hr prior to use.

SECTION 4

PROCEDURE

CHROMATOGRAPHY

The first step in the development of each test procedure was experimental determination of a detection system to meet the sensitivity requirements (1 µg/liter DL*) for each one of the compounds to be analyzed in a given group. Those chromatographic columns and operating parameters were selected which would separate the compounds expected to co-occur in a given industrial waste sample. The separation had to be sufficient for quantitation while keeping the analysis time under 1 hr.

Because GC was considered to be a more common and less expensive technique than HPLC, GC procedures were first investigated. Many compounds, however, were known to be heat labile so these were investigated by HPLC. Chromatographic conditions in common use were investigated. Dilute standards in solvent were injected into the chosen chromatographic system. Retention time and response factors were calculated.

EXTRACTION AND CONCENTRATION

One-liter aliquots of deionized water at pH 7 were spiked with one or more analytes. Three consecutive extractions with 60 ml of methylene chloride were performed in a 2-liter separatory flask. Extracts were combined and passed through a drying column filled with 5 to 10 cm of anhydrous sodium sulfate. The dried extract was concentrated to less than 5 ml by Kuderna-Danish technique. Fifty milliliters of hexane was added to the extract, and it was reconcentrated to less than 10 ml final volume. This extract was chromatographically analyzed for recovery. Several compounds were found to require unique extraction conditions, as discussed in the section "Results and Discussion" (p. 8). A goal of 85% recovery was set for this step.

CLEANUP

Twenty grams (nominal) of activated Florisil were placed in a cleanup column and prewet with 60 ml of petroleum ether. The entire extract was added to the column. Initial studies were performed with four sequential 200-ml elutions of 6%, then 15%, then 50%, and finally 100% ethyl ether in

---

* DL = detection limit. Defined as five times the noise background when 5 µl of a 1-liter sample extract concentrate (5 ml, final volume) is analyzed.

petroleum ether. Fractions were separately concentrated and chromatographically analyzed for recovery.

Poor recoveries of certain compounds were solved by eluting with stronger solvent (acetone), deactivating the absorbent with water, or using a different absorbent (alumina).

STABILITY

One-liter aliquots of deionized water, fortified with given pesticides were stored in the light at room temperature and neutral pH for at least 7 days; then the compounds were extracted and concentrated according to the verified procedure. Losses during storage were documented, but no experiments were run to isolate the causes or determine satisfactory storage conditions.

APPLICATION TO WASTEWATER

Samples of process or final effluent wastewater were collected from plants which manufacture the compounds of interest. These were adjusted to near pH 7 and stored at 4°C in the dark until use. To serve as a realistic challenge to the preliminary method, aliquots were analyzed by procedures developed using deionized water. Spiked aliquots were also analyzed for recovery. Often such studies indicated problems in recovery or with chromatographic interference. As a result, modifications were initiated in chromatography, extraction,and cleanup.

SECTION 5

RESULTS AND DISCUSSION

Table 1 lists the multiresudiue methods developed and the 58 compounds studied. Method numbers were assigned by EPA for purpose of regulatory citation. The structures and CAS nomenclature for the compounds are given in Appendix A. In the following discussion the results for each procedural step are presented.

TABLE 1. COMPOUNDS STUDIED; GROUPED BY EPA METHOD NUMBERS

Method 604 - Phenols
- Dinoseb

Method 608 - Organochlorine Pesticides and PCB's
- Chlorobenzilate
- Chloroneb
- Chloropropylate
- Dibromochloropropane
- Etridiazole
- PCNB

Method 619 - Triazines
- Ametryn
- Atrazine
- Prometon
- Prometryn
- Propazine
- Simetryn
- Simazine
- Terbutylazine
- Terbutryn

Method 622 - Organophosphorus Pesticides
- Azinphosmethyl
- Bolstar
- Chloropyrifos
- Coumaphos
- Demeton-O
- Demeton-S
- Diazinon
- Dichlorvos
- Disulfoton
- Ethoprop

(continued)

TABLE 1 (continued)

Fensulfothion
Fenthion
Mevinphos
Naled
Parathion, methyl
Phorate
Ronnel
Stirofos
Trichloronate

Method 623
4,4'-methylene bis(2-chloroaniline) [MOCA]

Method 628
Carbofuran

Method 629
Cyanazine

Method 631
Carbendazim and benomyl

Method 632 - Carbamate and Urea Pesticides
Diuron
Fluormetron
Linuron
Methomyl
Oxamyl
Propachlor
Propoxur

Method 633 - Organonitrogen Pesticides
Bromacil
DEET
Hexazinone
Metribuzin
Terbacil
Triadmefon
Tricyclazole

Method 634
Piperalin

Method 635
Piperonyl butoxide

Method number assignment pending
Aldicarb
Tokuthion

CHROMATOGRAPHY

The chromatographic columns, detectors, and operating parameters were selected to separate and detect specified groups of compounds in the presence of one another and other interferences associated with the wastewater analyzed.

The chromatographic conditions, detection limits, and retention times for each compound are summarized in Table 2. The compounds whose separation was considered during column and operating parameter selection are listed in the last column. All GC analyses were performed with 2-mm x 1.8-m ID glass columns with the exceptions noted for the first 10 organophosphorus compounds listed for Method 622. The 1-m column and rapid program rate were used in this instance to reduce on-column residence time for azinphosmethyl, which apparently decomposed on the longer column.

Initially an attempt was made to develop an HPLC method for the analysis of aldicarb in manufacturer's wastewater. The extraction efficiency, 7-day stability and column chromatography cleanup data were satisfactory for deionized water and hexane fortified with aldicarb. However, when the wastewater was extracted and the residue eluted from a Florisil column, the background interferences persisted and prevented the quantitation of aldicarb. Modification of the HPLC method from an isocratic system to a gradient system was also unsuccessful in obtaining the necessary resolution of aldicarb from the background. At this point, MRI began adapting a gas chromatographic residue method for the analysis of the wastewater.

In order to analyze aldicarb by gas chromatography, the compound was first oxidized to aldicarb sulfone by treatment with peracetic acid. The aldicarb sulfone was then thermally degraded in the injection port to produce the volatile species 2-methyl-2-(methylsulfonyl) propionitrile.

Two sets of operating parameters are given for cyanazine, dinoseb, and DEET. The second cyanazine method using HPLC was required to separate a wastewater interference which could not be removed by solid sorbent cleanup techniques. Method 604, developed prior to this work, was specified for the analysis of dinoseb. In the absence of interfering phenols, analysis time was reduced by operating at 160°C isothermal. A thermionic nitrogen specific detector, which might also improve sensitivity, was not evaluated for this analysis. It should be noted that gas chromatography of dinoseb is demanding. The column must be properly conditioned and devoid of active sites. Wastewater interferences required modification of the isothermal conditions initially developed for the analysis of DEET. Temperature programming was required to effect the necessary separation. Figures 2 through 33 (pp. 26 through 57) are copies of the GC or HPLC chromatograms of standard solutions of the studied compounds. The detection limit goals of 1 µg/liter GC and 10 µg/liter HPLC were met for 51 of the 58 compounds.

EXTRACTION AND CONCENTRATION

The goal of 85% extraction efficiency was met for 95% of the studied compounds. All the studied compounds were successfully extracted from water at pH 7 with three 60-ml portions of methylene chloride with the exception of

TABLE 2. CHROMATOGRAPHIC SYSTEMS AND PARAMETERS DEVELOPED FOR STUDIED COMPOUNDS

Method	Compound	Detection limit[a] (µg/ℓ)	Detector	Column	Operating parameters	Retention time (volume)	Chromatography developed for additional compounds
604	Dinoseb	20	FID[b]	1% SP-1240 DA on Supelcoport 100/120	10°/min program from 80-180° 10 min hold at 180° or, 160° isothermal	15.8 min 13.5 min	no
608	Chloroneb	0.001	ECD[c]	1% SP-2250 on Supelcoport 100/120	150° isothermal	10 min	no
	Chlorobenzilate	0.001	ECD	1.5% SP-2250, 1.95% SP-2401 on Supelcoport 100/120	215° isothermal	3.78 min	Chloropropylate
	Chloropropylate	0.001	ECD	1.5% SP-2250, 1.95% SP-2401 on Supelcoport 100/120	215° isothermal	3.66 min	Chlorobenzilate
	Dibromochloropropane	0.001	ECD	1.5% SP-2250, 1.95% SP-2401 on Supelcoport 100/120	100° isothermal	3.1 min	no
	Etridiazole	0.003	ECD	1.5% SP-2250, 1.95% SP-2401 on Supelcoport 100/120	140° isothermal	1.3 min	no
	PCNB	0.02	ECD	1.5% SP-2250, 1.95% SP-2401 on Supelcoport 100/120	160° isothermal	3.1 min	no
619	Ametryn	0.06	TSD[d]	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	17.7 min	Ametryn Atrazine Prometryn Propazine Simetryn Simazine Terbutylazine Terbutryn
	Atrazine	0.03	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	12.4 min	Same as above
	Prometon	0.03	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	6.9 min	Same as above
	Prometryn	0.03	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	13.8 min	Same as above

(continued)

TABLE 2 (continued)

Method	Compound	Detection[a] limit (µg/ℓ)	Detector	Column	Operating parameters	Retention time (volume)	Chromatography developed for additional compounds
	Propazine	0.03	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	9.2 min	Same as above
	Simetryn	0.07	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	23.0 min	Same as above
	Simazine	0.05	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	16.3 min	Same as above
	Terbutylazine	0.03	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	10.2 min	Same as above
	Terbutryn	0.05	TSD	5% Carbowax 20M-TPA on 100/120 Supelcoport	200° isothermal	15.4 min	Same as above
622	Azinphosmethyl	1.5	FPD[e]	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	6.8 min	Azinphosmethyl Bolstar, coumaphos, demeton-O, demeton-S, disulfoton, fensulfothion fenthion, phorate, trichloronate
	Bolstar	0.15	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	4.2 min	Same as above
	Coumaphos	1.5	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	11.6 min	Same as above
	Demeton-O	0.25	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	2.5 min	Same as above
	Demeton-S	0.25	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	1.2 min	Same as above

(continued)

TABLE 2 (continued)

Method	Compound	Detection[a] limit (µg/ℓ)	Detector	Column	Operating parameters	Retention time (volume)	Chromatography developed for additional compounds
	Disulfoton	0.20	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	2.1 min	Same as above
	Fensulfothion	1.5	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	6.4 min	Same as above
	Fenthion	0.1	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	3.1 min	Same as above
	Phorate	0.15	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	1.4 min	Same as above
	Trichloronate	0.15	FPD	5% SP-2401 on 100/120 Supelcoport	1 min at 150°, 25°/min increase to 220°, 9 min hold at 220° (1 meter column length)	2.9 min	Same as above
	Chloropyrifos	0.3	FPD	5% SP-2401 on 100/120 Supelcoport	10°/min increase from 160 to 220°	5.8 min	Ronnel
	Ronnel	0.3	FPD	5% SP-2401 on 100/120 Supelcoport	10°/min increase from 160 to 220°	4.9 min	Chloropyrifos
	Stirofos	0.5	FPD	5% SP-2401 on 100/120 Supelcoport	2 min hold at 170° 20°/min increase to 220°, hold for 10 min	8.5 min	Stirofos Mevinphos Dichlorvos Naled
	Naled	0.5	FPD	5% SP-2401 on 100/120 Supelcoport	2 min hold at 170° 20°/min increase to 220°, hold for 10 min	3.0 min	Stirofos Mevinphos Dichlorvos Naled
	Mevinphos	0.3	FPD	5% SP-2401 on 100/120 Supelcoport	2 min hold at 170° 20°/min increase to 220°, hold for 10 min	2.4 min	Stirofos Mevinphos Dichlorvos Naled
	Dichlorvos	0.1	FPD	5% SP-2401 on 100/120 Supelcoport	2 min hold at 170° 20°/min increase to 220°, hold for 10 min	0.8 min	Stirofos Mevinphos Dichlorvos Naled

(continued)

TABLE 2 (continued)

Method	Compound	Detection[a] limit (µg/ℓ)	Detector	Column	Operating parameters	Retention time (volume)	Chromatography developed for additional compounds
	Diazinon	0.8	FPD	5% SP-2401 on 100/120 Supelcoport	190° isothermal	2 min	no
	Ethoprop	0.03	FPD	5% SP-2401 on 100/120 Supelcoport	190° isothermal	1.2 min	no
	Parathion, methyl	0.8	FPD	5% SP-2401 on 100/120 Supelcoport	190° isothermal	9 min	no
623	MOCA	1.0	TSD	3% SP-2250 DB on 100/120 Supelcoport	260°C	4.4 min	no
628	Carbofuran	5	HPLC-UV 280 nm	µBondapak C_{18}	50:50 $CH_3CN:H_2O$ 2 ml/min	3.5 min (7 ml)	no
629	Cyanazine	0.04	TSD	3% SP-2250 on 100/120 Supelcoport	230°	5.2 min	Ametryn, Atrazine Prometon, Prometryn Propazine, Simetryn Simazine, Terbutylazine Terbutryn
		6	HPLC-UV 254 nm	µBondapak C_{18}	50:50 $H_2O:CH_3OH$ 1 ml/min	10.2 min (10.2 ml)	
631	Carbendazim and benomyl	3	HPLC-UV 280 nm	µBondapak C_{18}	50:50 $H_2O:CH_3OH$ 2 ml/min	3.9 min (7.8 ml)	
632	Diuron	0.3	HPLC-UV 254 nm	µBondapak C_{18}	10% CH_3CN/H_2O to 100% CH_3CN, linear gradient in 30 min with 2 ml/min flow	15.5 min (31 ml)	Methomyl, Linuron
	Linuron	0.3	HPLC-UV 254 nm	µBondapak C_{18}	10% CH_3CN/H_2O to 100% CH_3CN, linear gradient in 30 min with 2 ml/min flow	17.9 min (35.8)	Methomyl, Diuron
	Methomyl	3.5	HPLC-UV 254 nm	µBondapak C_{18}	10% CH_3CN/H_2O to 100% CH_3CN, linear gradient in 30 min with 2 ml/min flow	6.5 min (13 ml)	Diuron, Linuron
	Propachlor	16	HPLC-UV 254 nm	µBondapak C_{18}	50:50 $H_2O:CH_3CN$ 2 ml/min	4.7 min (9.4)	No
	Propoxur	16	HPLC-UV 280 nm	µBondapak C_{18}	50:50 $H_2O:CH_3CN$ 2 ml/min	3.4 min (6.8 ml)	No

(continued)

TABLE 2 (continued)

Method	Compound	Detection[a] limit (µg/ℓ)	Detector	Column	Operating parameters	Retention time (volume)	Chromatography developed for additional compounds
	Fluometuron	0.5	HPLC-UV 254 nm	µBondapak C_{18}	50:50 H_2O:CH_3CN 2 ml/min	3.6 min (7.2 ml)	No
	Oxamyl	1.5	HPLC-UV 254 nm	µBondapak C_{18}	25:75 CH_3OH:H_2O 1 ml/min	8 min (8 ml)	No
633	Metribuzin	0.7	TSD	3% SP-2401 on 100/120 Supelcoport	240° isothermal	2.4 min	Triadmefon
	Triadmefon	0.7	TSD	3% SP-2401 on 100/120 Supelcoport	240° isothermal	4.1 min	Metribuzin
	DEET	0.1	TSD	3% SP-2401 on 100/120 Supelcoport	180° isothermal	1.6 min	No
					1 min at 130° 12°/min increase to 200°	4.6 min	Developed for wastewater interferences
	Tricyclazole	0.1	TSD	3% SP-2250 DB on 100/120 Supelcoport	240° isothermal	3.5 min	
	Bromacil	0.2	TSD	3% SP-2250 DB on 100/120 Supelcoport	2 min at 210° 10°/min increase to 250°	3.7 min	Terbacil Hexazinone
	Hexazinone	0.5	TSD	3% SP-2250 DB on 100/120 Supelcoport	2 min at 210° 10°/min increase to 250°	7.6 min	Bromacil Terbacil
	Terbacil	0.5	TSD	3% SP-2250 DB on 100/120 Supelcoport	2 min at 210° 10°/min increase to 250°	2.1 min	Hexazinone Bromacil
634	Piperalin	0.3	TSD	3% SP-2340 on Supelcoport 100/120	200°, isothermal	3.2 min	No
635	Piperonyl butoxide	6	HPLC-UV 280 nm	µBondapak C_{18}	65% CH_3CN:35% H_2O 1.5 ml/min	14.3 ml (9.5 min)	No
*	Aldicarb	0.4	TSD	5% Carbowax 20M-TPA on Supelcoport 80/100	150°, isothermal	2.5 min	No
		5	HPLC-UV 254 nm	µBondapak C_{18}	(1) 50% CH_3CN:50% H_2O 2 ml/min	5.6 min	No
					(2) 20% CH_3CN/H_2O to 70% CH_3CN/H_2O Linear gradient in 20 min, 2 ml/min	18.1 min	No
*	Tokuthion	0.5	FPD	5% SP-2401 on Supelcoport 100/120	1 min hold at 150° 25°/min increase to 220° 9 min hold at 220° (1 m column length)	3.4 min	Yes

a Detection limit - nanograms needed to give a signal 10 times the noise level.

b FID - flame ionization detector.

c ECD - electron capture detector.

d TSD - thermionic nitrogen specific detector.

e FPD - flame photometric detector.

* EPA method number to be assigned.

carbendazim and benomyl and dinoseb. An increase in solvent volume from 60 to 350 ml resulted in an increase in the recovery of carbendazim from 15 to 83%. Since benomyl slowly hydrolyzes to carbendazim,[2] it was decided to develop the method for benomyl around the total conversion to carbendazim. One liter of neutral wastewater and 10 ml of HCl were stirred for 24 hr to assure the complete hydrolysis of benomyl to carbendazim. The pH was then raised to 7 for sample extraction with three 350-ml portions of methylene chloride.

The previously developed test procedure for phenols (604) was evaluated for the analysis of Dinoseb. Method 604 requires an initial extraction (3 x 60 ml CH_2Cl_2) at pH 11 to remove basic interferences and a final extraction at pH 2 for the partitioning of Dinoseb and other acidic phenols.

As discussed in the previous section, aldicarb was oxidized to aldicarb sulfone for chromatographic purposes. Prior to extraction the water was treated with peracetic acid and allowed to stand 15 min. The oxidized sample was neutralized with 10% sodium bicarbonate and then extracted with three 60-ml portions of methylene chloride. The combined extracts were concentrated and taken completely to dryness, until no peracetic acid odor remained. This must be done to eliminate background interferences during the GC/TSD analysis.

Two significant losses of piperalin occurred during the sample workup procedure. The first of these losses involved the extract drying step and is presumably dependent upon the activity and amount of the anhydrous sodium sulfate used to dry the methylene chloride extract. Studies showed that recovery of piperalin from a water-saturated methylene chloride extract after drying with a 10-cm column of anhydrous sodium sulfate (~ 20 g) was quantitative. However, when a dry extract spiked with piperalin was passed through a similar column, a recovery of about 35% was observed. No specific studies were undertaken to determine the maximum amount of sodium sulfate which could be used in drying an extract; however, a 10-cm (~ 20 g) column proved to be adequate to dry the extract and not cause any significant losses of piperalin. Alternatively, the drying step could be eliminated and the final solvent exchange could be made into acetone rather than hexane.

The second and perhaps most dramatic loss of piperalin during the sample workup occurred during the solvent evaporation step. Silanization of the two lower portions of the Kuderna-Danish evaporator was necessary to prevent adsorption of any piperalin present in the extract to the surface of the glass. Studies indicated that adsorption of piperalin to unsilanized glass surfaces occurred only during the extract concentration step and not during the extraction or extract drying step.

STABILITY

Deionized water fortified with each compound was extracted on day 0 and day 7 after storage at ambient conditions and neutral pH. The percent recovery values are included in Table 3. Comparison of the two values would indicate a need for some means of preservation for Bolstar, Demeton-S, Disulfoton, Fenthion, Phorate, Trichloronate, Ronnel, Dichlorovos. tokuthion, and piperalin. It should be noted, however, that no effort was made to determine the cause of analyte losses during storage.

TABLE 3. EXTRACTION EFFICIENCY AND 7-DAY STABILITY RESULTS

Method	Compound	Concentration (µg/ℓ)	% Recovery Day 0	% Recovery Day 7
604	Dinoseb	100	94, 95	92
608	Chloroneb	5	87, 73	70
	Chlorobenzilate	5	96	96
	Chloropropylate	5	91	94
	Dibromochloropropane	5	86, 84	84
	Etridiazole	1	99	100
	PCNB	1	68	65
619	Ametryn	1	103, 100	90
	Atrazine	1	101, 101	92
	Prometon	1	96, 99	94
	Prometryn	1	96, 101	93
	Propazine	1	97, 100	94
	Simetryn	1	102, 102	93
	Simazine	1	94, 103	91
	Terbutylazine	1	95, 102	96
	Terbutryn	1	93, 93	93
622	Azinphosmethyl	1	96	87
	Bolstar	1	100	79
	Coumaphos	1	99	97
	Demeton-O	1	91	75
	Demeton-S	1	97	0
	Disulfoton	1	111	71
	Fensulfothion	1	102	91
	Fenthion	1	87	61
	Phorate	1	89	29
	Trichloronate	1	107	55
	Chloropyrifos	1	78	70
	Ronnel	1	91	58
	Stirofos	1	83	80
	Naled	1	95	91
	Mevinphos	1	92	88
	Dichlorvos	1	110	70
	Diazinon	1	91	89
	Ethoprop	1	101	100
	Parathion, methyl	1	99	94
623	MOCA	200	80	90
		10	55	ND[a]
		5	56	ND[a]
628	Carbofuran	10	101, 101	102
629	Cyanazine	1	88, 101	94
631	Carbendazim	10	83	ND[a]
	Benomyl	150	81, 72	ND[a]

(continued)

TABLE 3 (continued)

Method	Compound	Concentration (µg/ℓ)	% Recovery Day 0	% Recovery Day 7
632	Diuron	10	95, 89	93
	Linuron	10	91, 92	96
	Methomyl	100	78, 77	95
	Propachlor	100	104, 109	104
	Propoxur	100	91, 89	91
	Fluometuron	10	98, 87	99
	Oxamyl	10	98	82
633	Metribuzin	1	95, 100	102, 88
	Triadmefon	1	93, 93	88
	DEET	1	97	96
	Tricyclazole	1	100, 100	81
	Bromacil	1	91	100
	Hexazinone	1	102	83
	Terbacil	1	97	99
634	Piperalin	1	95	60
635	Piperonyl butoxide	10	96, 102	87
*	Aldicarb	1	70, 72	60
*	Tokuthion	1	92, 95	63

a ND - value not determined.

* EPA method number to be assigned.

CLEANUP

Since manufacturer's wastewater generally contains structurally similar compounds (i.e., starting materials, by-products and degradation products) the development of a cleanup for extracts of this matrix is most important but is also most difficult.

Modifications of the preliminary cleanup procedure were made when necessary and possible. In some cases GC or LC parameters were varied instead of or in addition to modifying the cleanup system in order to achieve adequate resolution from the wastewater interferences. Column materials and elution mixtures were evaluated using the predetermined order given in Table 4. Because of the use of selective detector systems, it was only necessary to cleanup the extracts of seven wastewaters representative of 13 of the 58 studied compounds. It was observed that the adsorptivity varied greatly between determinations made with fortified hexane and actual wastewater extracts. It is advisable to retain all fractions and determine the elution pattern of the compound in the presence of any new set of matrix interferences. Chromatograms of wastewater extracts before and after cleanup are shown in Figure 34 to 40 (pp. 58 through 64).

TABLE 4. COLUMN CLEANUP SYSTEMS

System no.	Solid sorbent	Elution mixtures	Percentages
1	Florisil	Ethyl ether/petroleum ether	6, 15, 50, 100
2	Florisil	Acetone/hexane	6, 15, 50, 100
3	2% water deactivated Florisil	Acetone/hexane	6, 15, 50, 100
4	6% water deactivated Florisil	Acetone/hexane	6, 15, 50, 100
5	10% water deactivated Alumina	Ethyl ether/petroleum ether	6, 15, 50, 100

Since the existing phenol Method 604 evaluated for dinoseb does not include a cleanup step, no method was developed.

Triazines containing the functional group S-CH_3 could be successfully recovered only from 10% deactivated alumina. Although nonsulfonated triazines, with the exception of cyanazine, were recovered from Florisil with ether-petroleum ether, the alumina column was used because both types of triazine were present in the wastewater.

Organophosphorus pesticides as a class exhibited extremely poor recovery from Florisil. Because of the specificity of the flame photometric detector

solid sorbent cleanup was not required in the analysis of wastewater, and only system 1 was evaluated for those compounds because of time considerations.

All the solid sorbent cleanup systems given in Table 4 were evaluated for piperalin. None were successful due to 100% retention of piperalin by the adsorbents.

No cleanup method was developed or required for the analysis of MOCA.

Satisfactory recovery of labile compounds such as carbamates and ureas generally required substitution of the more polar acetone/hexane mixture as would be expected. No solid sorbent technique was successful in both recovering cyanazine and removing the interferences which appeared in a relevant wastewater. An HPLC method was developed for this purpose.

Caution must be used when attempting to apply a cleanup developed for one matrix to another matrix.

Table 5 summarizes the recovery results from solid sorbents and indicates which compounds were determined in wastewater without the need for cleanup.

WASTEWATER ANALYSES

When possible, wastewater was obtained from industrial sites that manufactured one or more of compounds studied. These water samples were utilized to allow for needed method modifications due to matrix effects and to verify the efficiency of final procedures. First, the preliminary method developed with fortified reagents was tested on a relevant sample and any necessary changes were made. Percent recovery values for the final procedure were then determined on wastewater that had been fortified with levels relevant to those observed in the background. Table 6 provides recovery data at specified spiking levels.

TABLE 5. PERCENT RECOVERY OF STUDIED COMPOUNDS FROM SELECTED SOLID SORBENT CLEANUP SYSTEMS

Method	Compound	System[a]	Added amount (µg)	% Recovery by fraction					Total Recovery	Required for wastewater
				6	15	50	100[a]	100[b]		
604	Dinoseb			NOT DEVELOPED						
608	Chloroneb	1	10	93	-	-	-	-	93	yes
	Chlorobenzilate	1	10	-	15	70	-	-	85	yes
	Chloropropylate	1	10	-	32	61	-	-	93	yes
	Dibromochloropropane	1	10	60	10	1	-	-	71	yes
	Etridiazole	1	1	100	-	-	-	-	100	yes
	PCNB	1	1	75	-	-	-	-	75	yes
619	Ametryn	1	1	-	-	7	-	-	7	no
		5	1	-	70	21	-	-	91	
	Atrazine	1	1	-	3	93	-	-	96	no
		5	1	-	99	-	-	-	99	no
	Prometon	1	1	-	-	-	66	-	66	no
		5	1	-	84	-	-	-	84	
	Prometryn	1	1	-	7	3	-	-	10	no
		5	1	-	13	98	-	-	111	
	Propazine	1	1	-	58	33	-	-	91	no
		5	1	-	53	41	-	-	94	
	Simetryn	1	1	-	-	-	23	-	23	no
		5	1	-	89	-	-	-	89	
	Simazine	1	1	-	-	92	-	-	92	no
		5	1	-	94	-	-	-	94	
	Terbutylazine	1	1	-	16	75	-	-	91	no
		5	1	-	35	57	-	-	92	
	Terbutryn	1	1	-	-	-	-	-	0	no
			1	-	-	85	-	-	85	
622	Azinphos methyl	1	1	-	-	-	33	-	33	no
	Bolstar	1	1	35	-	-	-	-	35	no
	Coumaphos	1	1	-	-	-	44	-	44	no
	Demeton-O	1	1	-	-	-	-	-	0	no
	Demeton-S	1	4	-	-	-	-	-	0	no
	Disulfoton	1	1	26	16	10	-	-	52	no
	Fensulfothion	1	1	-	-	-	-	-	0	no
	Fenthion	1	1	16	9	-	-	-	25	no

(continued)

TABLE 5 (continued)

Method	Compound	System[a]	Added amount (µg)	% Recovery by fraction 6	15	50	100[a]	100[b]	Total Recovery	Required for wastewater
	Phorate	1	1	34	-	-	-	-	34	no
	Trichloronate	1	1	67	-	-	-	-	67	no
	Chloropyrifos	1	1	100	-	-	-	-	100	no
	Ronnel	1	1	82	-	-	-	-	82	no
	Stirofos	1	1	-	63	-	-	-	63	no
	Naled	1	1	-	-	-	-	-	0	no
	Mevinphos	1	1	-	-	-	14	-	14	no
	Dichlorvos	1	1	-	-	-	24	-	24	no
	Diazinon	1	1	-	30	36	10	-	76	no
	Ethoprop	1	1	-	-	-	70	-	70	no
	Parathion, methyl	1	1	-	-	90	-	-	90	no
623	MOCA					NOT DEVELOPED				
628	Carbofuran	1	10	-	-	43	61	-	104	no
629	Cyanazine	1	1	-	-	83	-	-	83	yes[b]
		5	1	-	29	-	-	-	29	
631	Carbendazim and benomyl	2	100	-	-	46	-	-	46	no
632	Diuron	2	10	-	24	58	-	-	82	no
	Linuron	2	10	14	82	-	-	-	96	no
	Methomyl	2	100	-	-	84	-	-	84	no
	Propachlor	6	100	94	-	-	-	-	94	yes
	Oxamyl	2	100	-	-	92	-	-	92	no
	Propoxur	1	100	-	-	-	89	-	89	yes
	Fluometuron	1	10	-	-	-	63	32	95	yes

(continued)

TABLE 5 (continued)

Method	Compound	System[a]	Added amount (µg)	% Recovery by fraction 6	15	50	100[a]	100[b]	Total	Required for wastewater
633	Metribuzin	3	1	22	45	-	-	-	67	yes
	Triadmefon	3	1	-	100	-	-	-	100	yes
	DEET	3	1	21	60	-	-	-	81	no
	Tricyclazole	3	1	20	22	35	18	-	101	no
	Hexazinone	4	1	-	-	82	-	-	82	no
	Terbacil	4	1	-	62	-	-	-	62	no
	Bromacil		1	-	10	38	-	-	48	no
634	Piperalin			Not Developed						
635	Piperonyl butoxide	2	10	10	-	-	-	-	100	yes
*	Aldicarb	2	1	-	-	86	-	-	86	no
*	Tokuthion	1	1	65	7	-	-	-	72	no

a

Systems	Sorbent	Elution mixture
1	Florisil	ether/petroleum ether 6, 15, 50, 100a, 100b
2	Florisil	acetone/hexane 6, 15, 50, 100
3	2% water deactivated Florisil	acetone/hexane 6, 15, 50, 100
4	6% water deactivated Florisil	acetone/hexane 6, 15, 50, 100
5	10% water deactivated Alumina Florisil	ether/petroleum ether 6, 15, 50, 100
6		20% ether/hexane, then 6, 15, 50, 100 acetone/hexane

b No solid sorbent evaluated was effective in removing a wastewater interference and analysis was completed by HPLC.

* EPA method number to be assigned.

TABLE 6. PERCENT RECOVERY OF STUDIED COMPOUNDS FROM RELEVANT WASTEWATER

Method	Compound	Manufacturing Site[a]	Influent Background (µg/ℓ)	Influent Added (µg/ℓ)	Influent % R	Effluent Background (µg/ℓ)	Effluent Added (µg/ℓ)	Effluent % R
604	Dinoseb	A	460	840	86, 98	30	420	69, 74
608	Chlorobenzilate	B	99	108	26, 48	5.2	4	118, 172
	Chloropropylate	B	< 1.0			< 1.0	10	129, 130
	Chloroneb	C	33	16	48	0.3	0.1	63
	Dibromochloropropane	D	< 0.005	1.2	74, 87	< 0.007	1.2	73, 32
	Etridiazole	E	0.010	1	81, 113	< 0.006	1	92, 100
	PCNB	E	50	100	20, 36	-	-	-
619	Ametryn	B	16,000	20,000	111, 96	31,000	40,000	125, 111
	Atrazine	B	1,500	1,500	115, 100	1,100	1,200	142, 129
	Prometon	B	140	150	126, 98	164	200	135, 117
	Prometryn	B	9,300	10,000	80, 72	955	1,000	123, 97
	Propazine	B	900	1,000	105, 77	280	300	122, 109
	Simetryn	B	130	150	198, 168	270	300	194, 169
	Simazine	B	420	500	122, 103	180	200	104, 93
	Terbutylazine	B	450	500	126, 101	230	300	105, 94
	Terbutryn	B	440	500	131, 103	140	200	91, 83
622	Azinphos methyl	F	*[b]	6	101	*[b]	6	69, 101
	Bolstar	F	*[b]	10	77, 111	*[b]	5	85, 94
	Coumephos	F	*[b]	9	131, 256	*[b]	9	213, 255
	Demeton-O	F	*[b]	8	95, 78	*[b]	8	72, 80
	Demeton-S	F	*[b]	2.6	17	*[b]	2.6	0, 0
	Disulfoton	F	*[b]	17	129, 141	*[b]	17	93, 93
	Fensulfothion	F	*[b]	360	89, 139	*[b]	360	72, 78
	Fenthion	F	*[b]	8	43, 41	*[b]	8	60, 42
	Phorate	F	*[b]	10	47	*[b]	10	57, 69
	Trichloronate	F	*[b]	15	51, 44	*[b]	15	34, 40
	Chloropyrifos	G	*[b]	3	97, 81	*[b]	3	104, 102
	Ronnel	G	*[b]	3	93, 80	*[b]	3	68, 60
	Diazinon	B	41	15	110, 137	1.1	4.3	108, 108
	Dichlorvos	D	< 2	4	120, 110	< 2	4	89, 110
	Mevinphos	D	< 2	4	86, 92	< 2	4	120, 78
	Naled	D	7.2	4	60, 80	< 2	4	95, 90
	Stirofos	D	< 2	4	110, 120	< 2	4	120, 98
623	MOCA	H	212	200	45, 56	< 1.0	20	87, 93
							10	79, 44

(continued)

TABLE 6 (continued)

Method	Compound	Manufacturing Site[a]	Influent Background (µg/ℓ)	Influent Added (µg/ℓ)	Influent % R	Effluent Background (µg/ℓ)	Effluent Added (µg/ℓ)	Effluent % R
628	Carbofuran	I	600,000	-	-	< 5	13	120, 108
629	Cyanazine	B	-		Insufficient sample for quantitation			
631	Carbendazim	J	8,000	-	-	190	230	138, 120
	Benomyl	C	164		Insufficient sample for quantitation			
632	Diuron	C	240	250	108, 212	110	100	91, 101
	Linuron	C	47	50	66, 130	21	50	56, 42
	Methomyl	C	300	250	148, 170	41	100	59, 55
	Fluormetron	B	880	1,460	90, 94	870	1,280	80, 76
	Oxamyl	J	-[b]	-	-	81[b]	200	93, 97
	Propachlor	G	*[b]	200	56, 68	*[b]	100	98, 89
	Propoxur	F	*[b]	100	63, 68	*[b]	100	71
633	Bromacil	C	5,990	6,450	102, 88	2,433	2,700	109, 126
	Hexazinone	C	1,715	2,000	137, 83	767	900	95, 108
	Terbacil	C	4,165	-	-	1,675	1,800	104, 119
	DEET	K	270,000[b]	270,000	110, 110	590	540	106, 103
	Metribuzin	F	*[b]	200	79, 41	*[b]	200	41, 50
	Triadmefon	F	*[b]	92	74, 63	*[b]	92	100, 94
	Tricyclazole	L	960	684	82, 74	< 0.2	0.8	94, 97
634	Piperalin	L	334[d]	375	75, 58	0[e]	7.1	
						0[f]	162, 101	95, 87
635	Piperonyl butoxide	K	270	240	103, 115	0	10	96, 101
**	Aldicarb	D	*[b] 47	50	28, 56[c]	*[b] 26	20	50, 50[c]
**	Tokuthion	F		21	43[c]		64	36[c]

a Identification of site on file at EMSL-Cin.

b Data on file at EMSL-Cin.

c Mean of triplicate analyses.

d Sample collection point designated only by number 7.

e Sample collection point designated only by number 4.

f Sample collection point designated only by number 6.

** EPA method number to be assigned.

REFERENCES

1. Federal Register, Vol. 44, No. 233, p. 69464 (December 3, 1979).

2. Austin, D. J., A. Lord, and I. H. Williams, Pesticide Science, Vol. 7, p. 211 (1976).

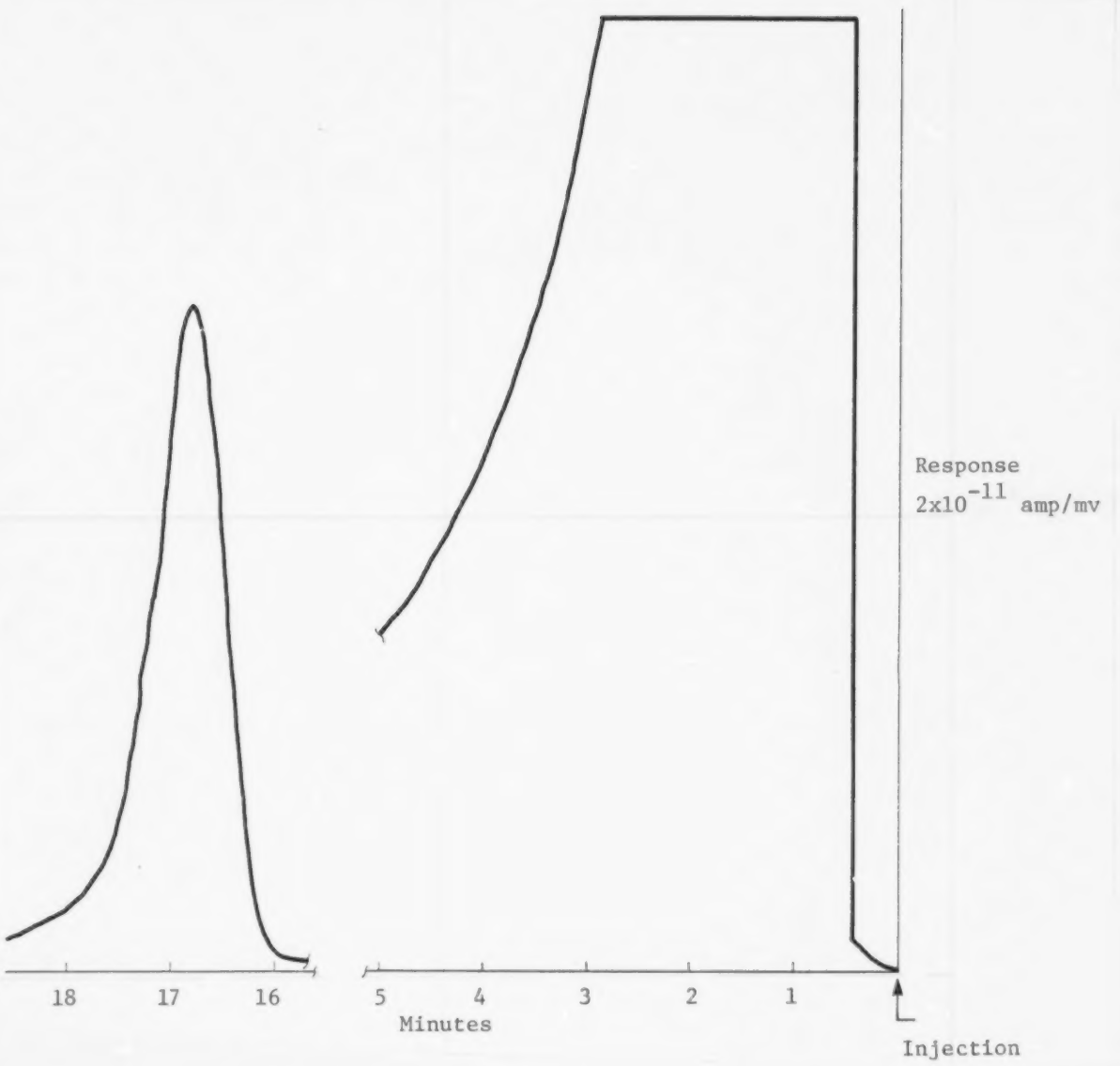


Figure 2. GC/FID chromatogram of the dinoseb standard (168 ng).

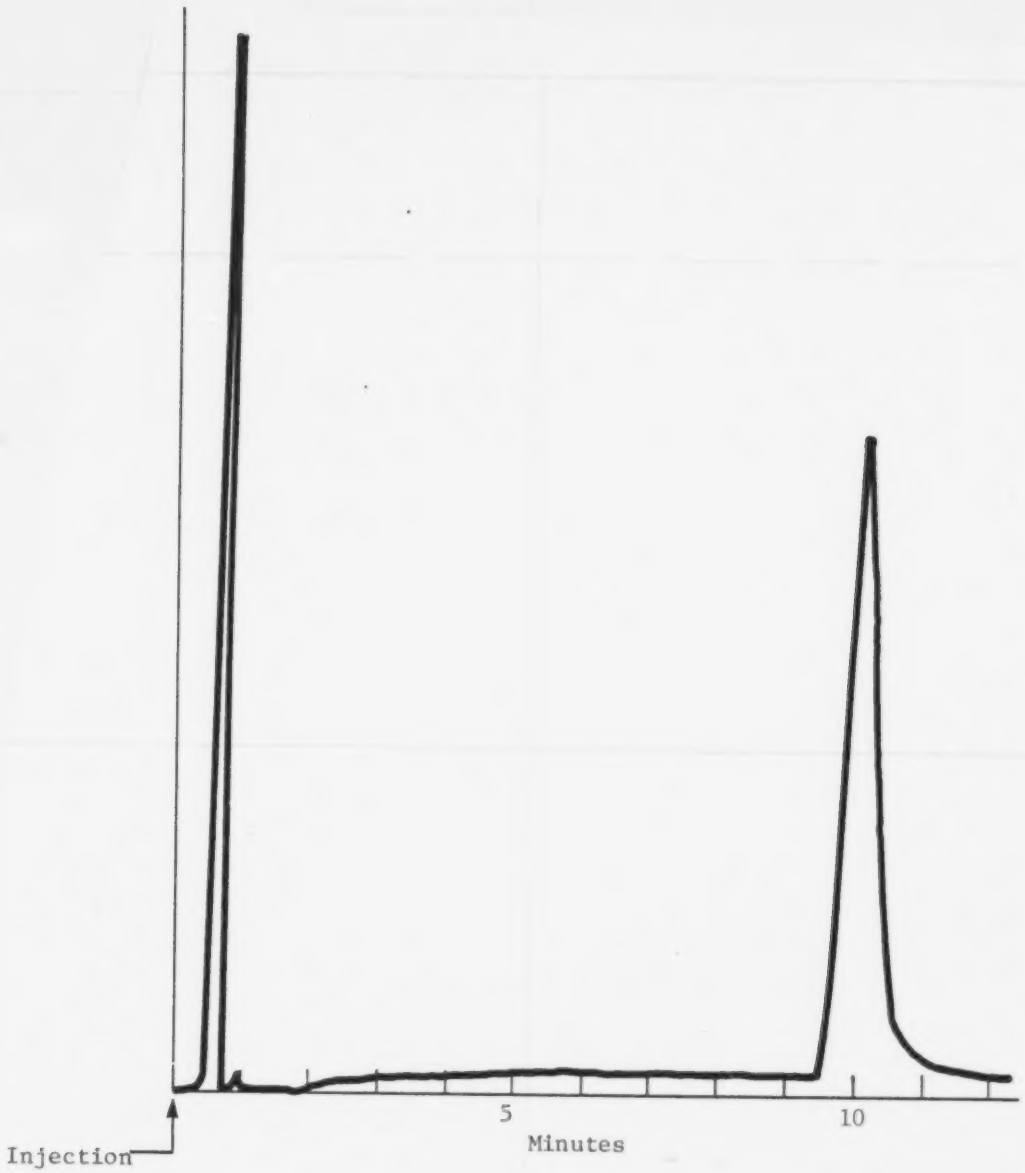


Figure 3. GC/ECD chromatogram of chloroneb standard (3 ng).

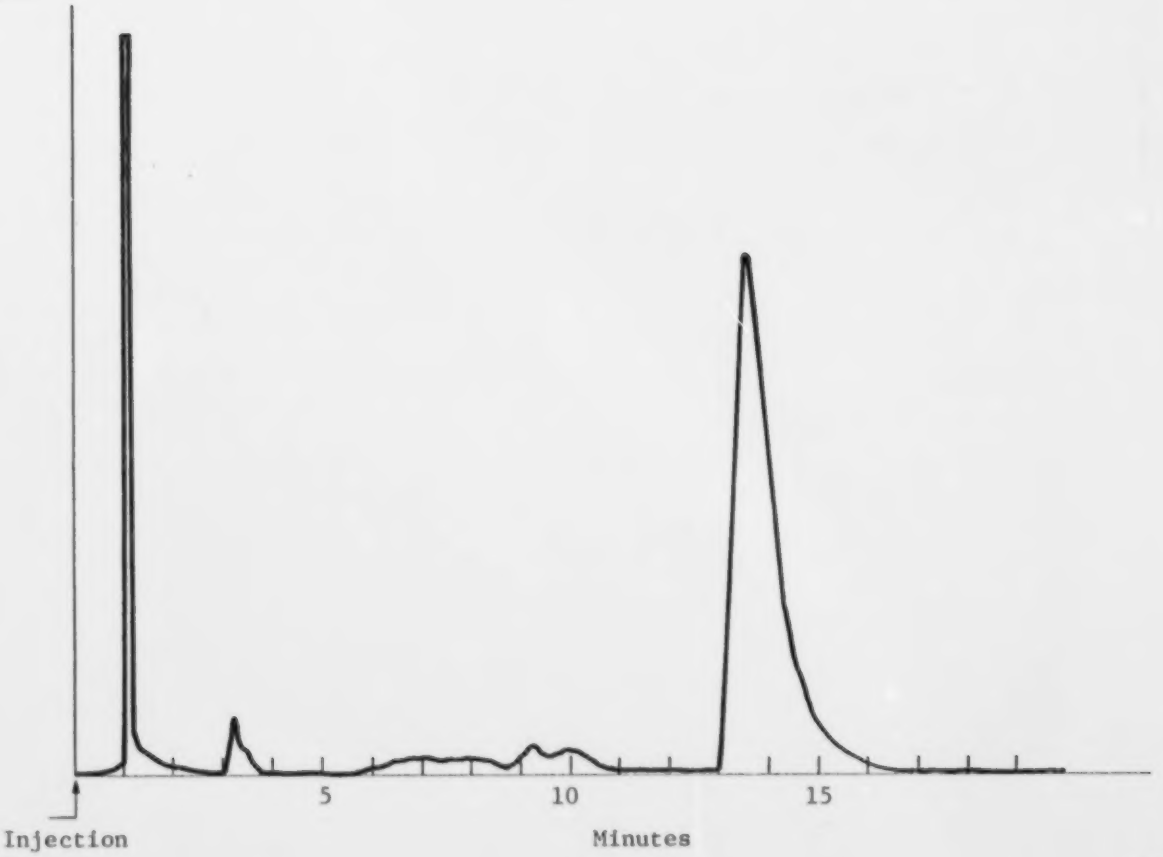


Figure 4. GC/ECD chromatogram of the chlorobenzilate standard (3 ng).

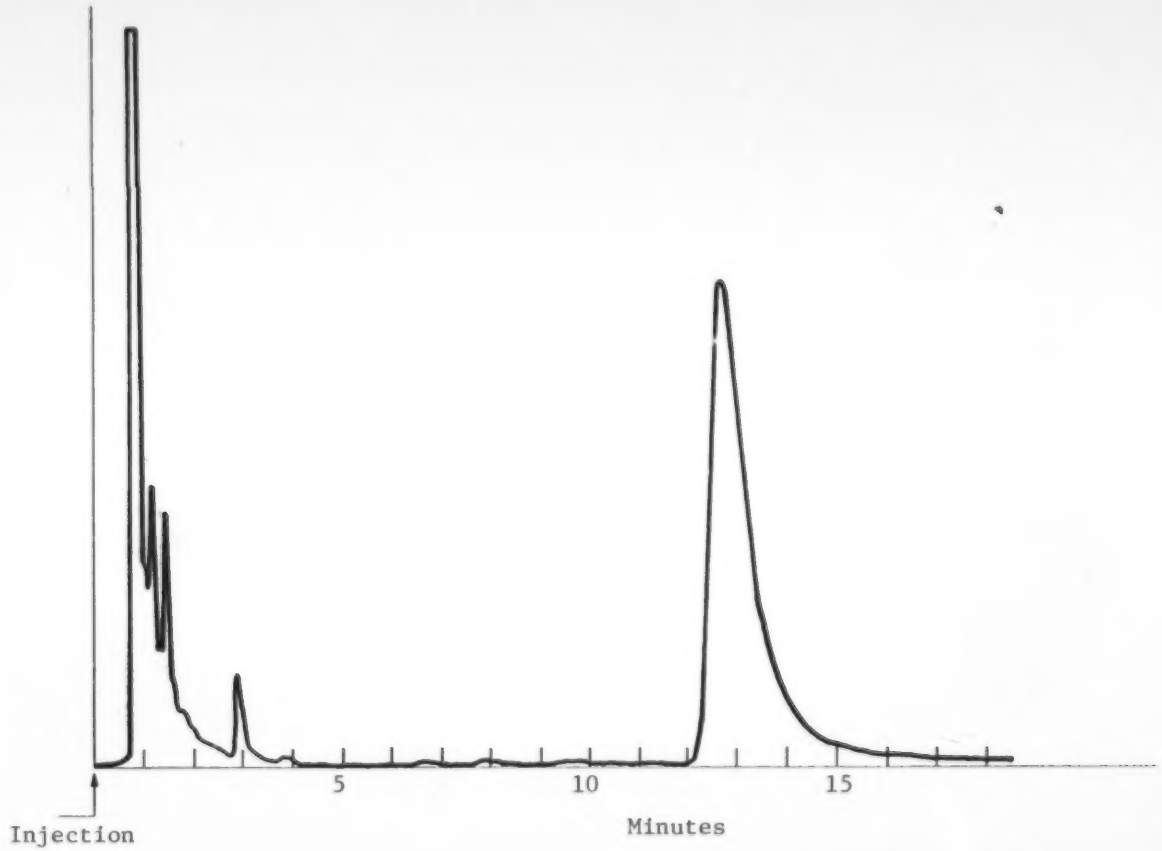


Figure 5. GC/ECD chromatogram of the chloropropylate standard (3 ng).

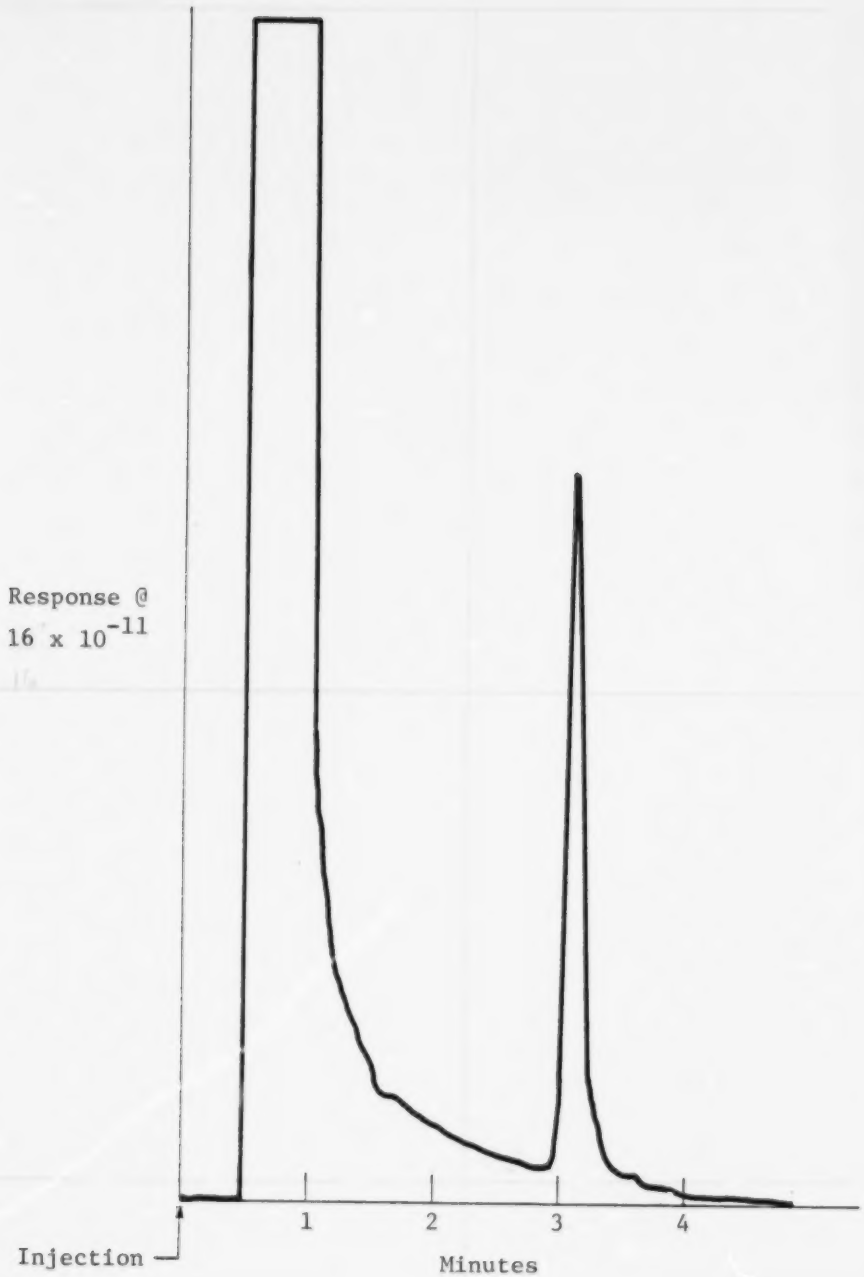


Figure 6. GC/ECD chromatogram of dibromochloropropane standard (0.3 ng).

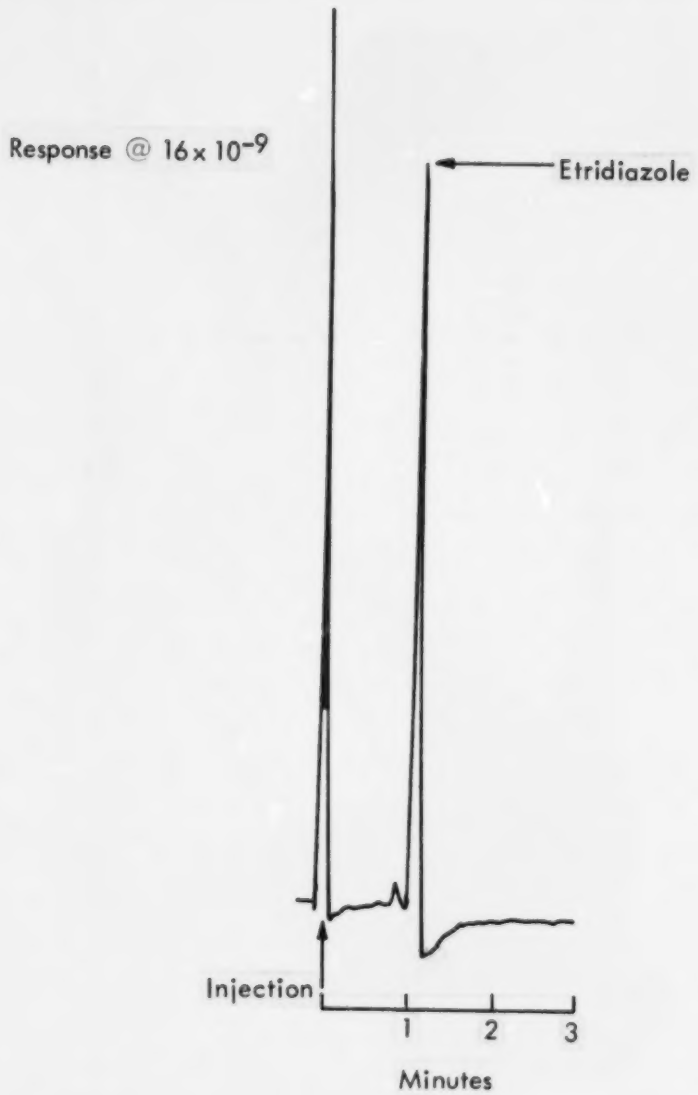


Figure 7. GC/EC chromatogram of etridiazole standard (100 pg).

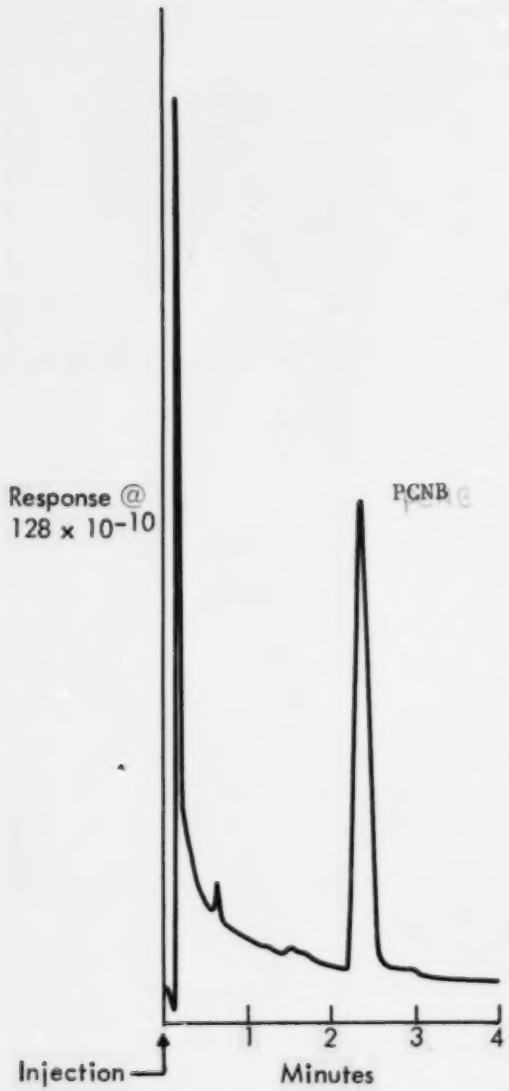


Figure 8. GC/EC chromatogram of pentachloronitrobenzene standard (1 ng).

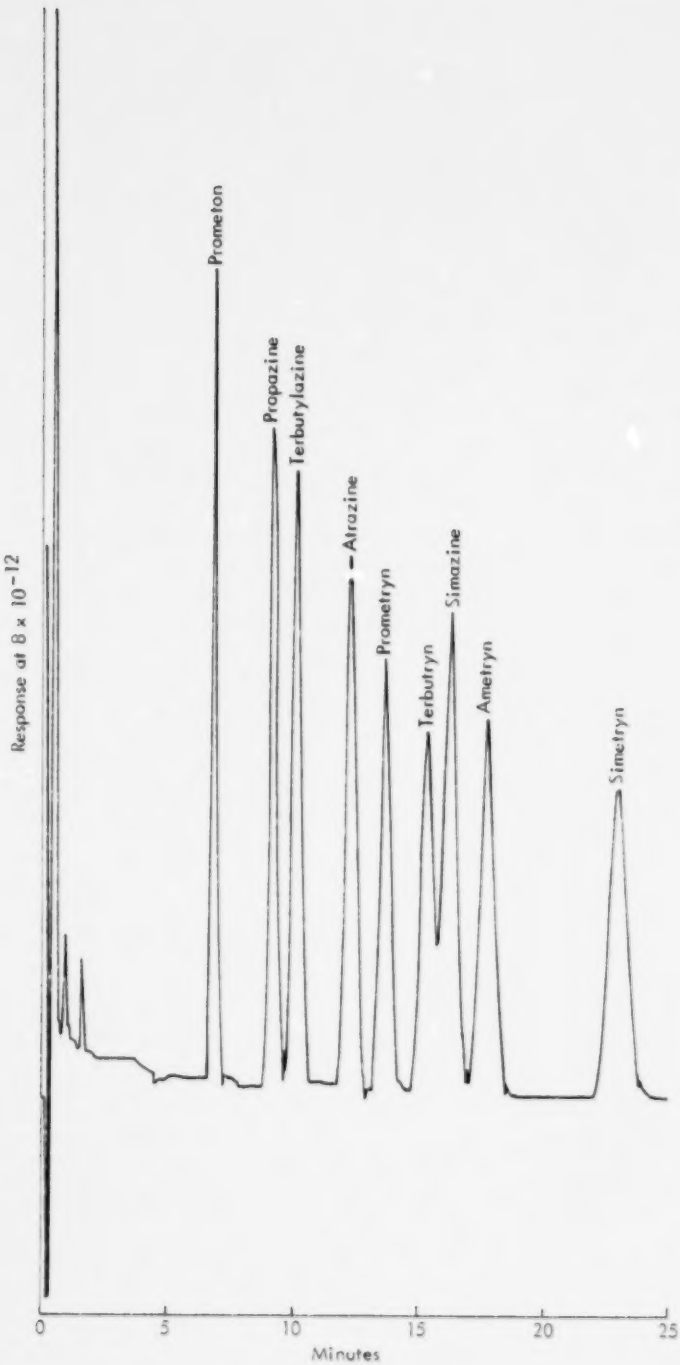


Figure 9. GC/TSD chromatogram of mixed triazine pesticide standard (1.1 ng) on a Carbowax column.

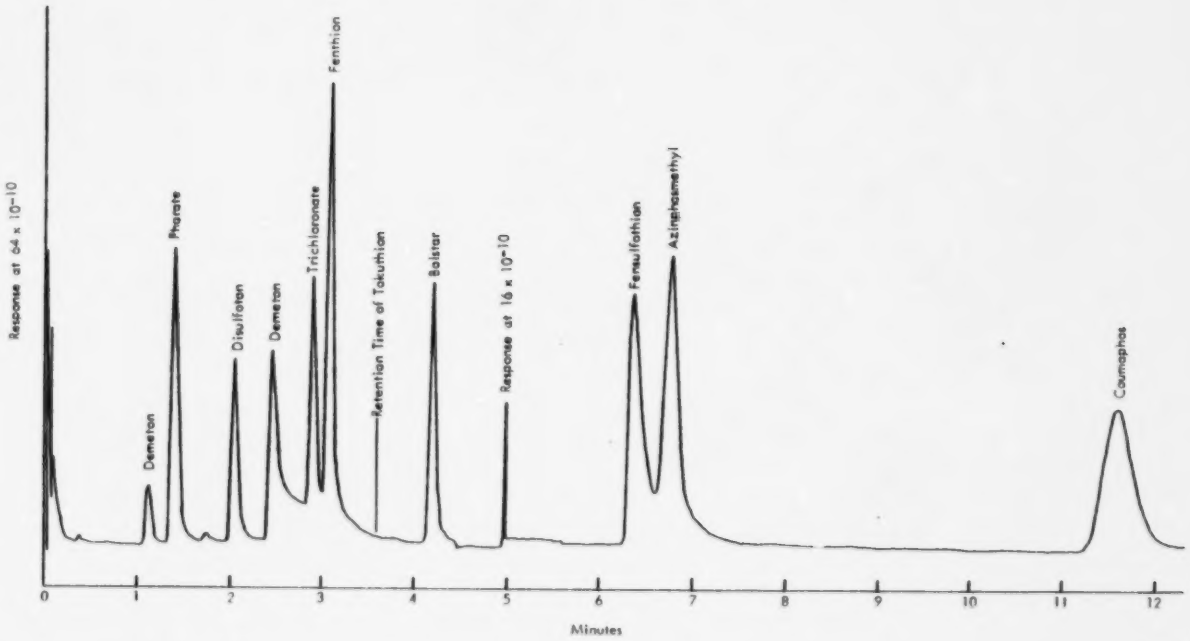


Figure 10. GC/FPD chromatogram of mixed organophosphorus pesticide standard (∿ 5 ng).

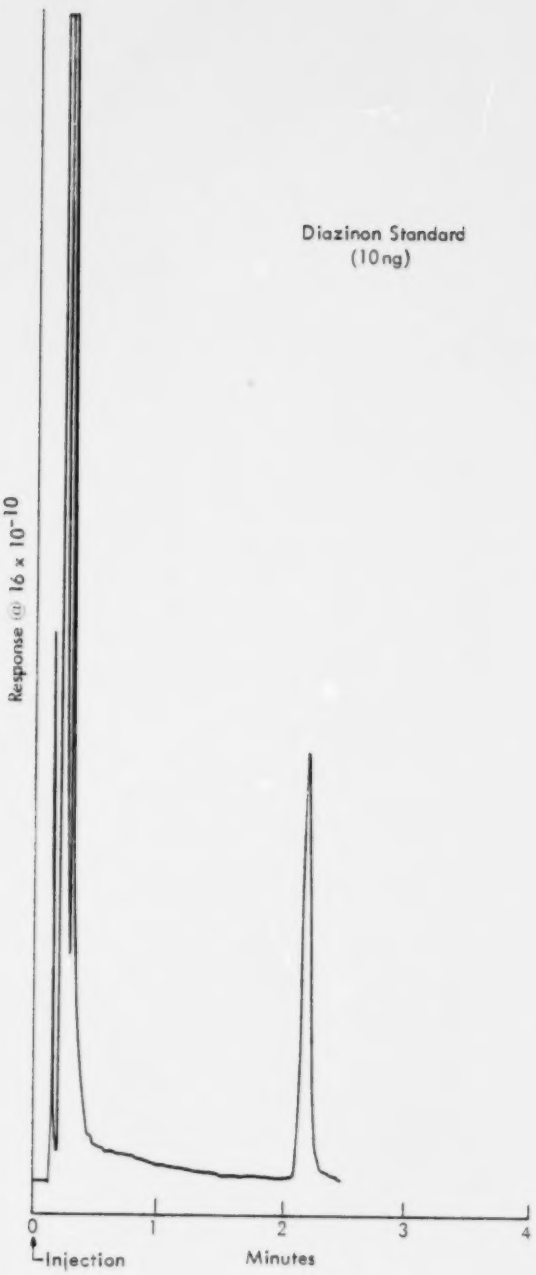


Figure 11. GC/FPD chromatogram of diazinon standard (10 ng).

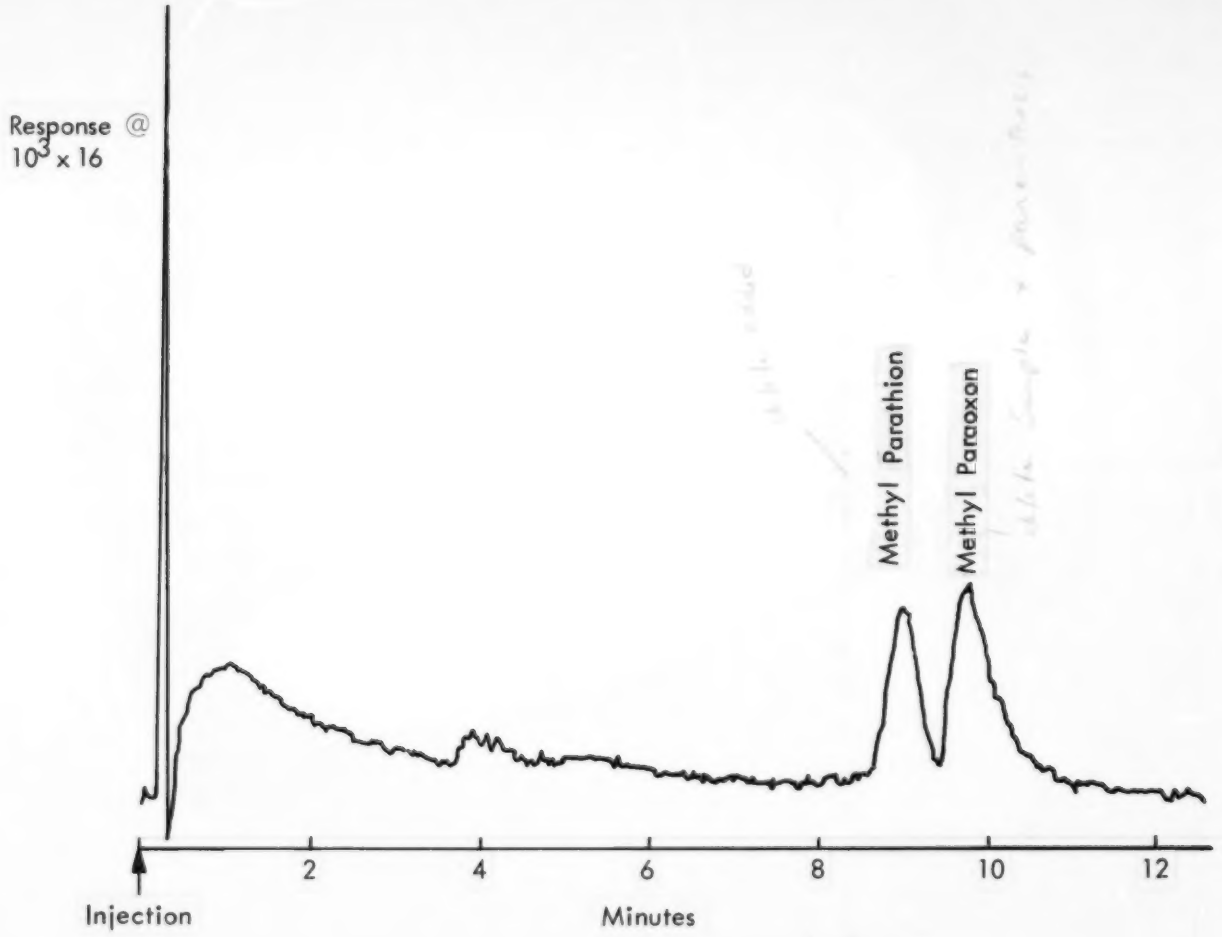


Figure 12. GC/FPD chromatogram of methyl parathion and methyl paraoxon.

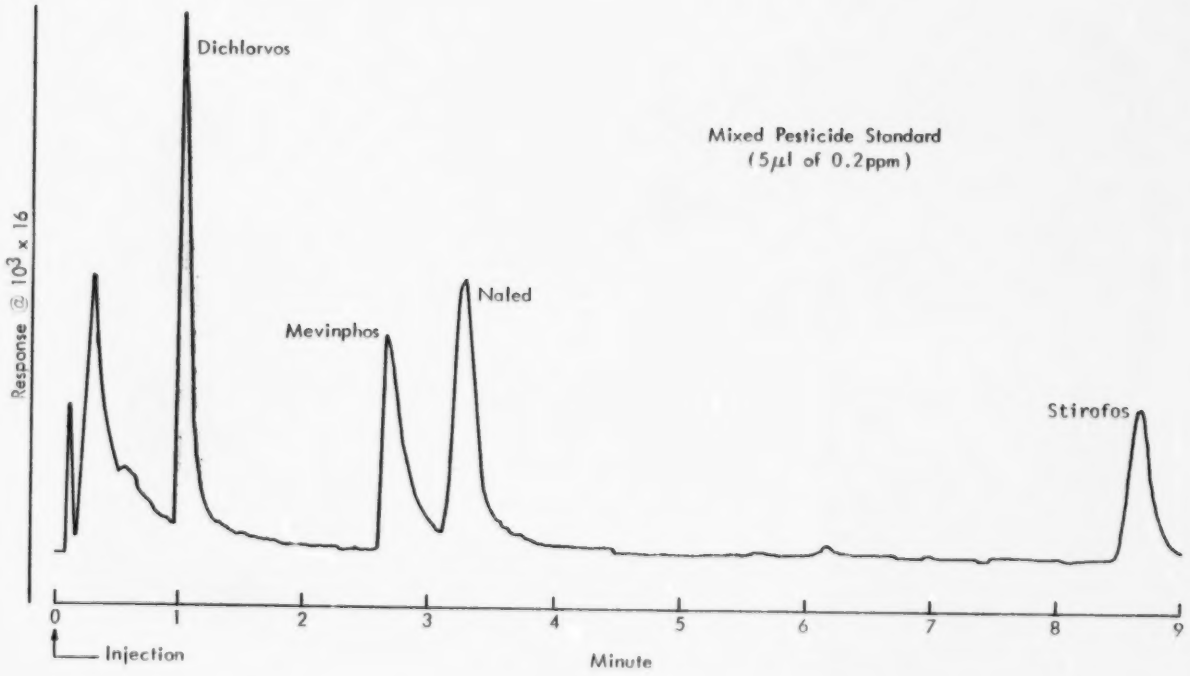


Figure 13. GC/FPD chromatogram of mixed pesticide standard (1 ng).

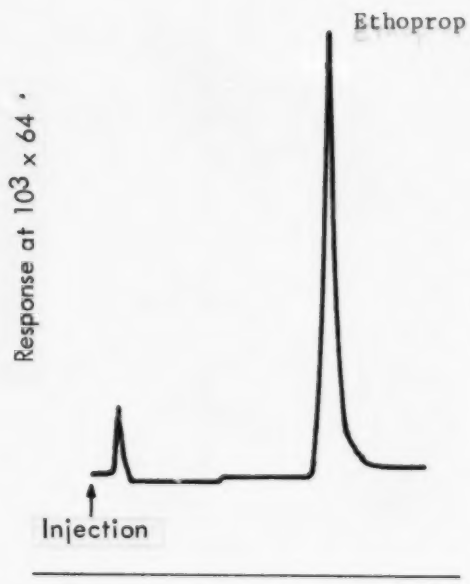


Figure 14. GC/FPD chromatogram of ethoprop standard (0.6 ng).

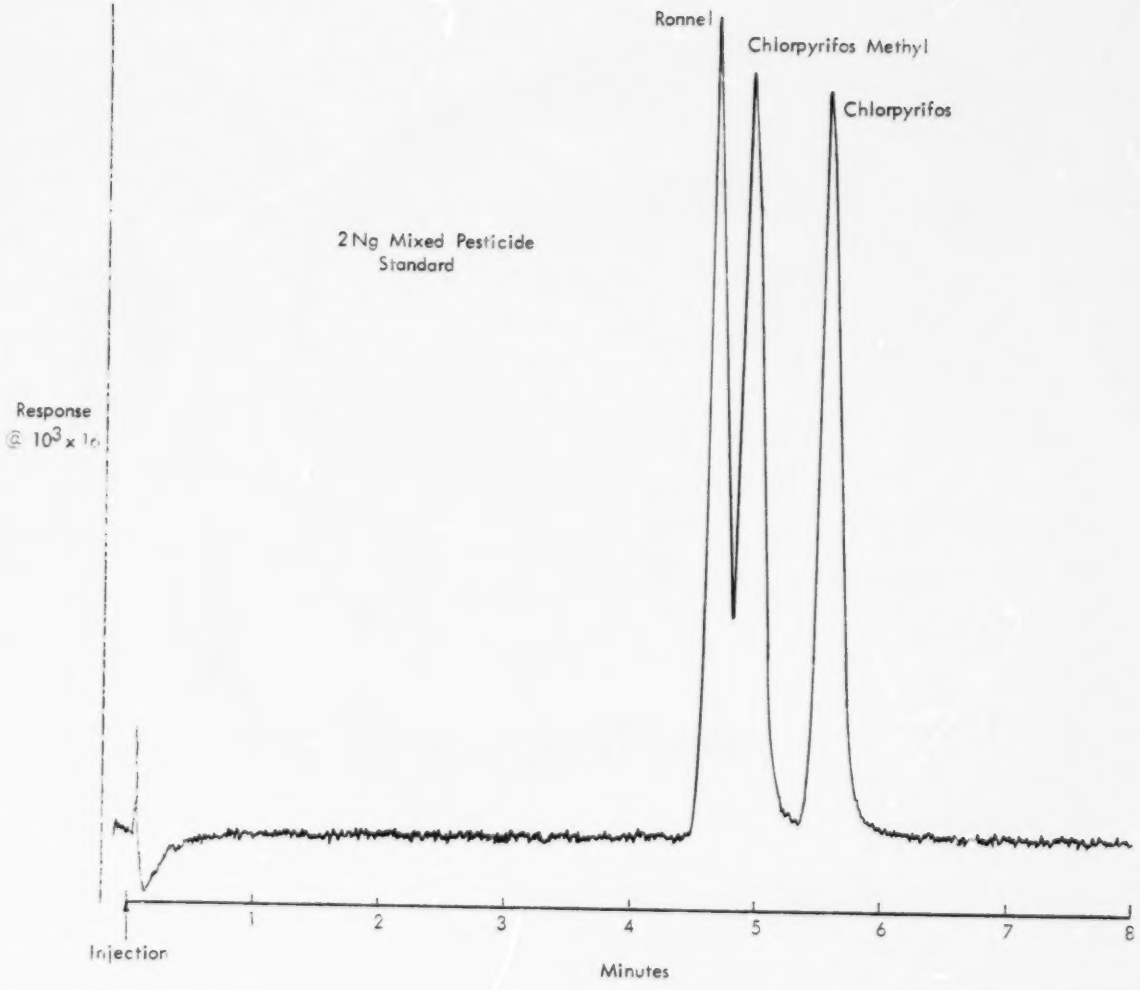


Figure 15. GC/FPD chromatogram of ronnel, chlorpyrifos methyl and chlorpyrifos standard (2 ng).

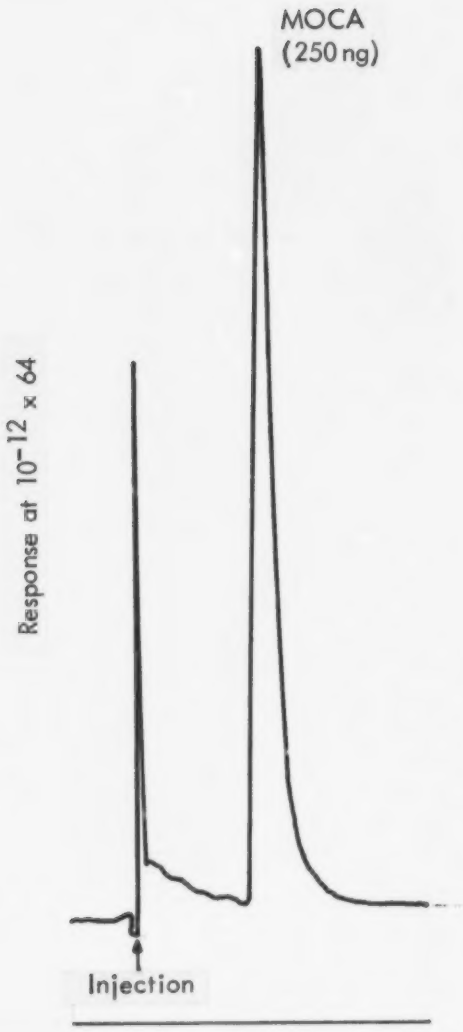


Figure 16. GC/TSD chromatogram of MOCA standard (250 ng).

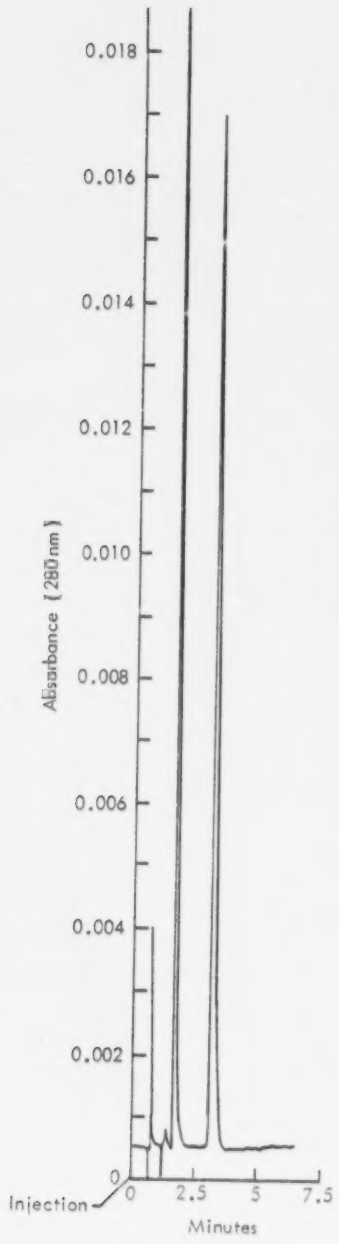


Figure 17. HPLC chromatogram of carbofuran standard (500 ng).

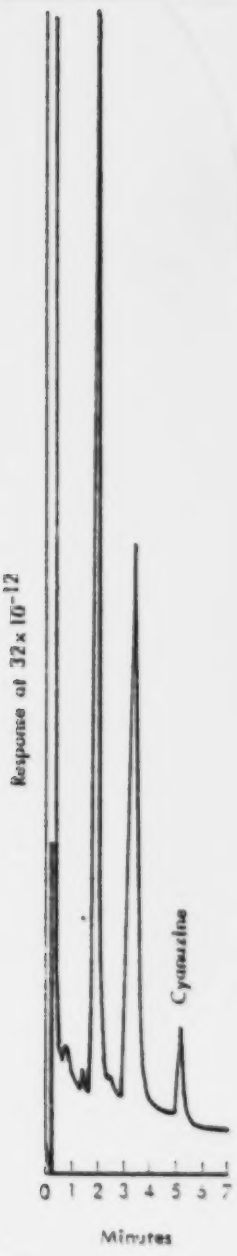


Figure 18. GC/TSD chromatogram of mixed tirazine standard (1.1 ng) on the SP-2250 column.

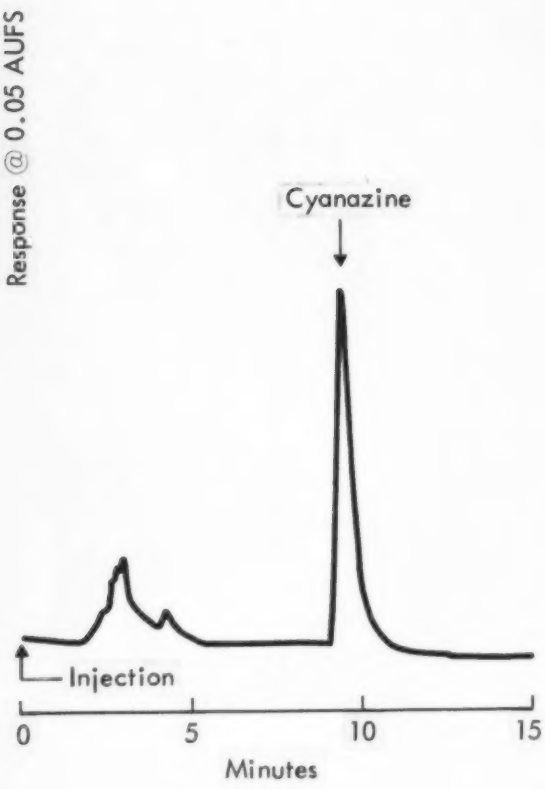


Figure 19. HPLC chromatogram of cyanazine standard (0.5 µg).

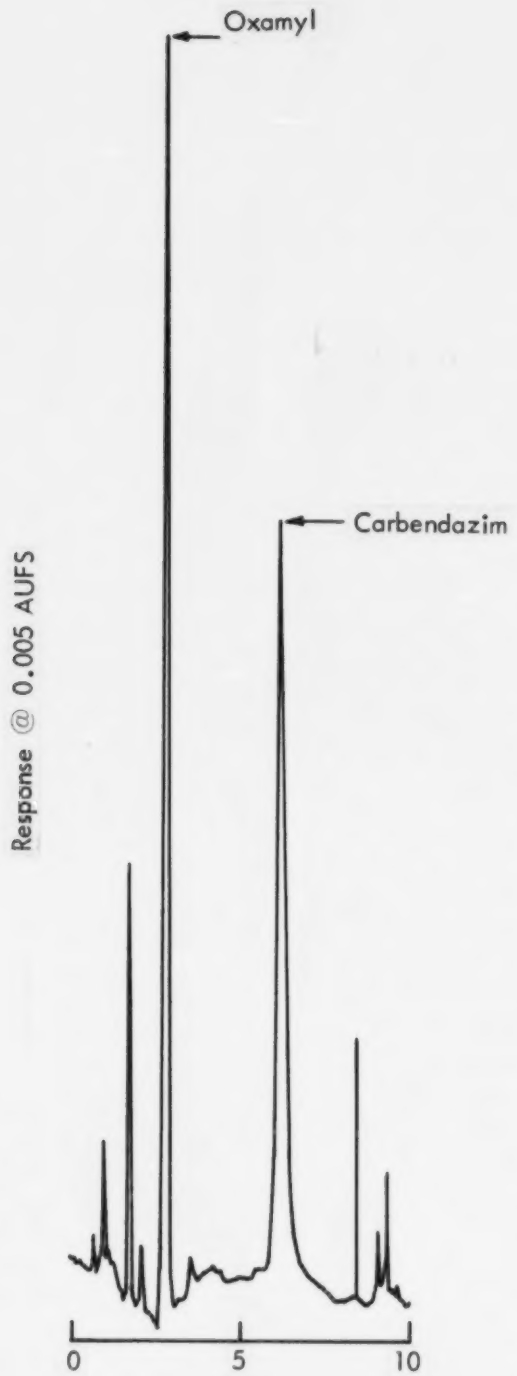


Figure 20. HPLC chromatogram of oxamyl and carbendazim standard (100 ng).

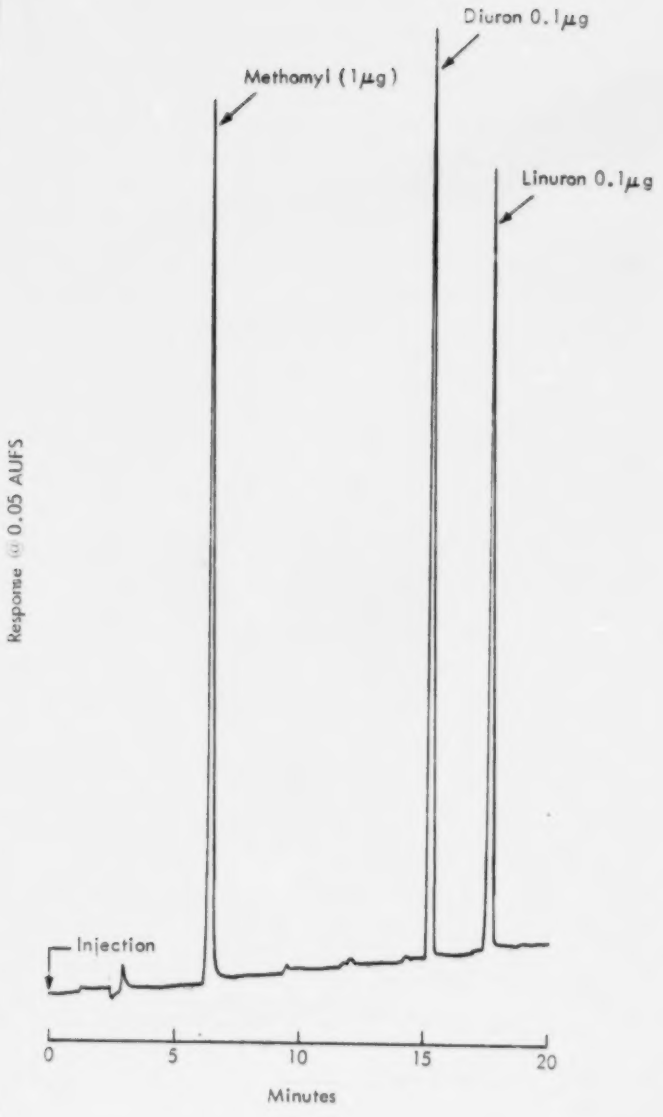


Figure 21. HPLC chromatogram of methomyl (1 µg), diuron (0.1 µg), and linuron (0.1 µg) standard.

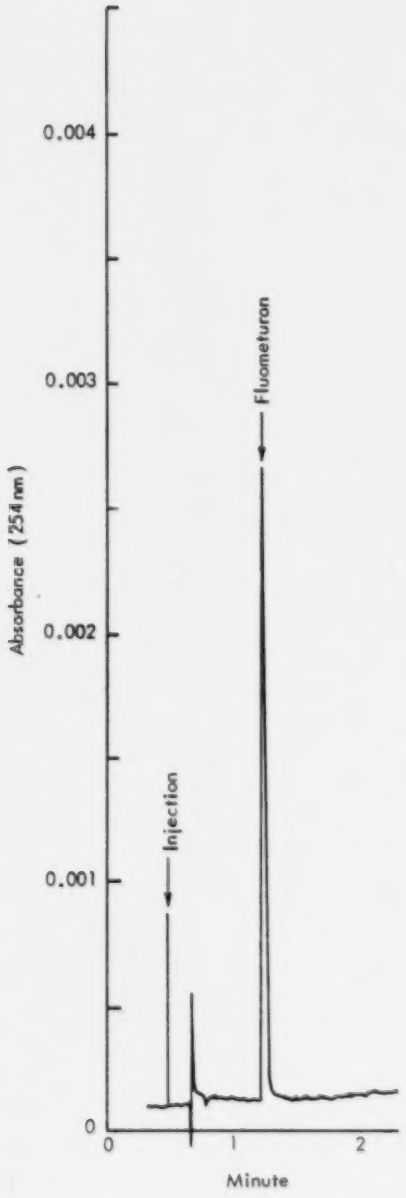


Figure 22. HPLC chromatogram of fluometuron standard (20 ng).

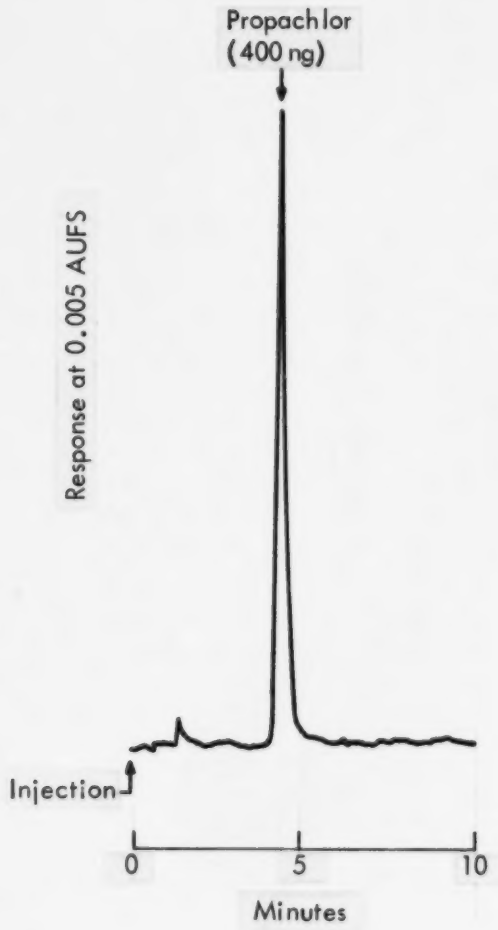


Figure 23. HPLC chromatogram of propachlor standard (400 ng).

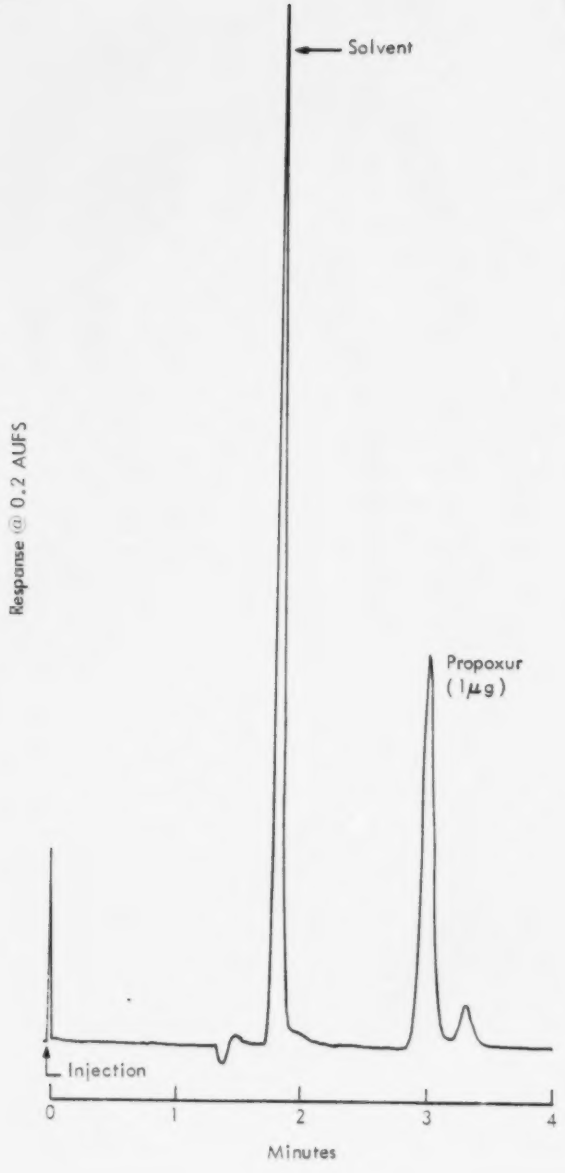


Figure 24. HPLC chromatogram of propoxur (1 μg).

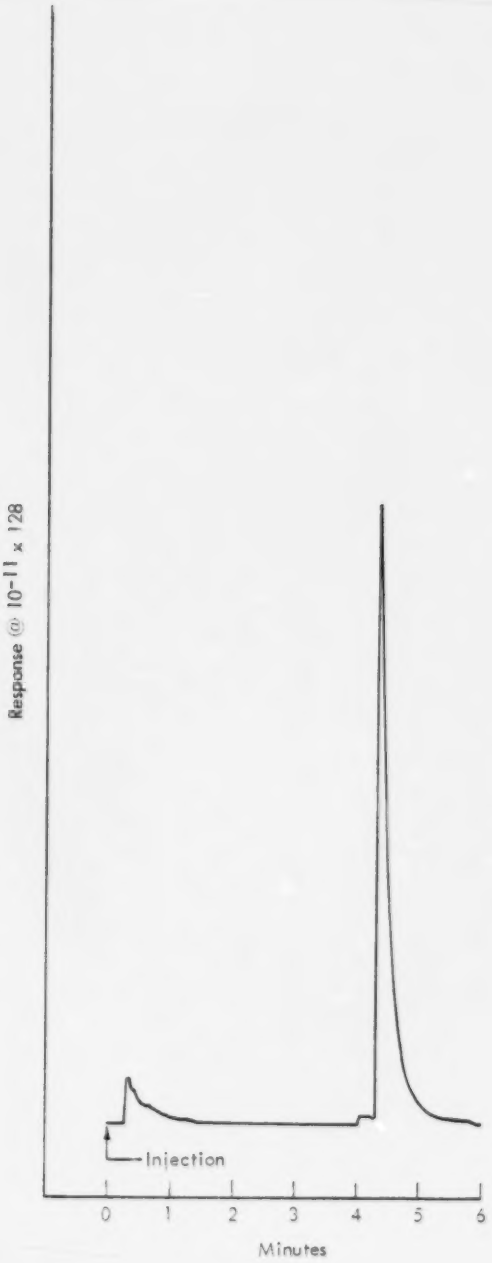


Figure 25. GC/TSD chromatogram of DEET standard (500 ng).

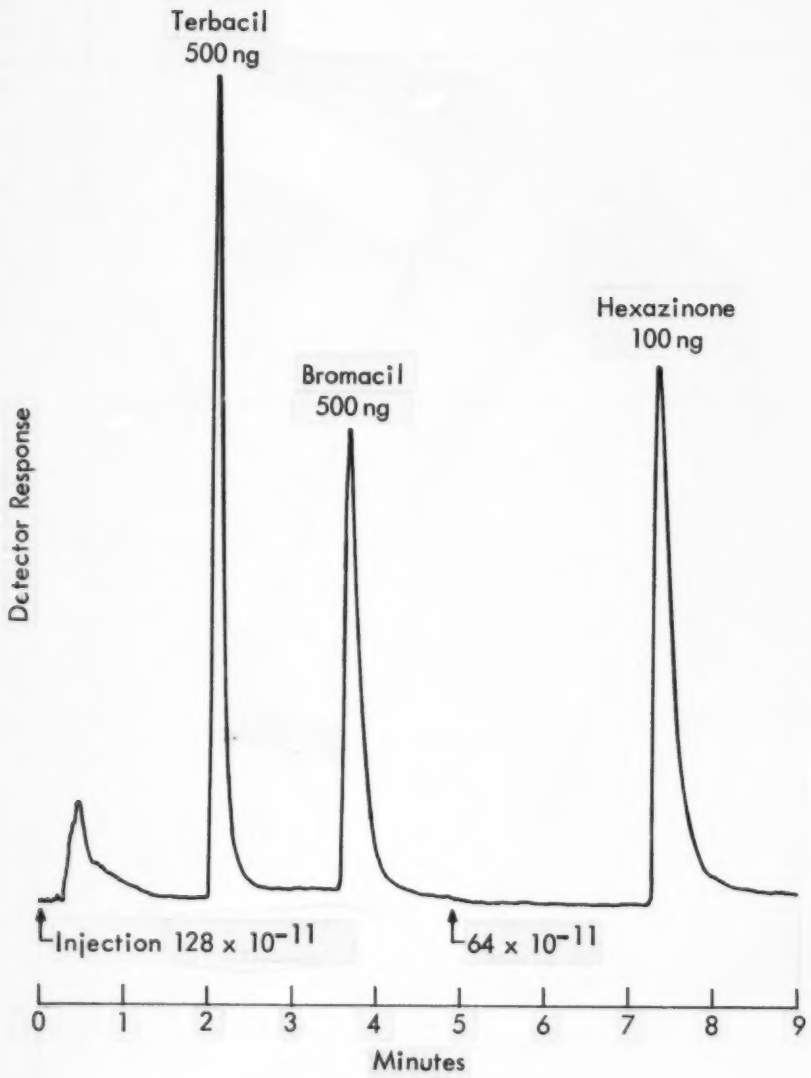


Figure 26. GC/TSD chromatogram of terbacil (500 ng), bromacil (500 ng), and hexazinone (100 ng) standard.

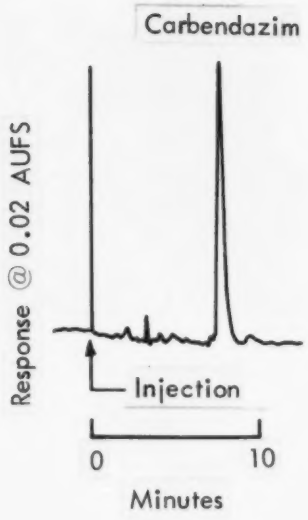


Figure 27. HPLC chromatogram of carbendazim standard (20 ng).

Figure 28, GC/TSD chromatogram of metribuzin (1.4 ng) and triadmefon (1.1 ng) standard.

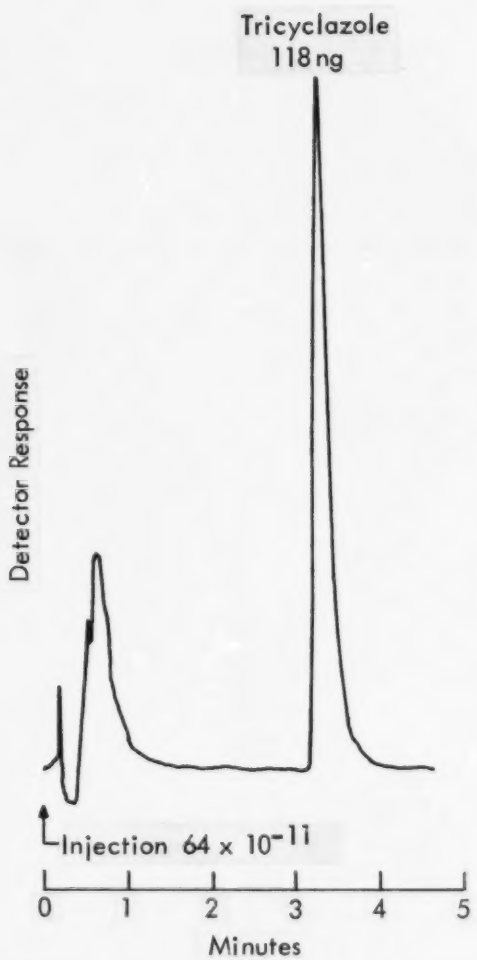


Figure 29. GC/TSD chromatogram of tricyclazole standard.

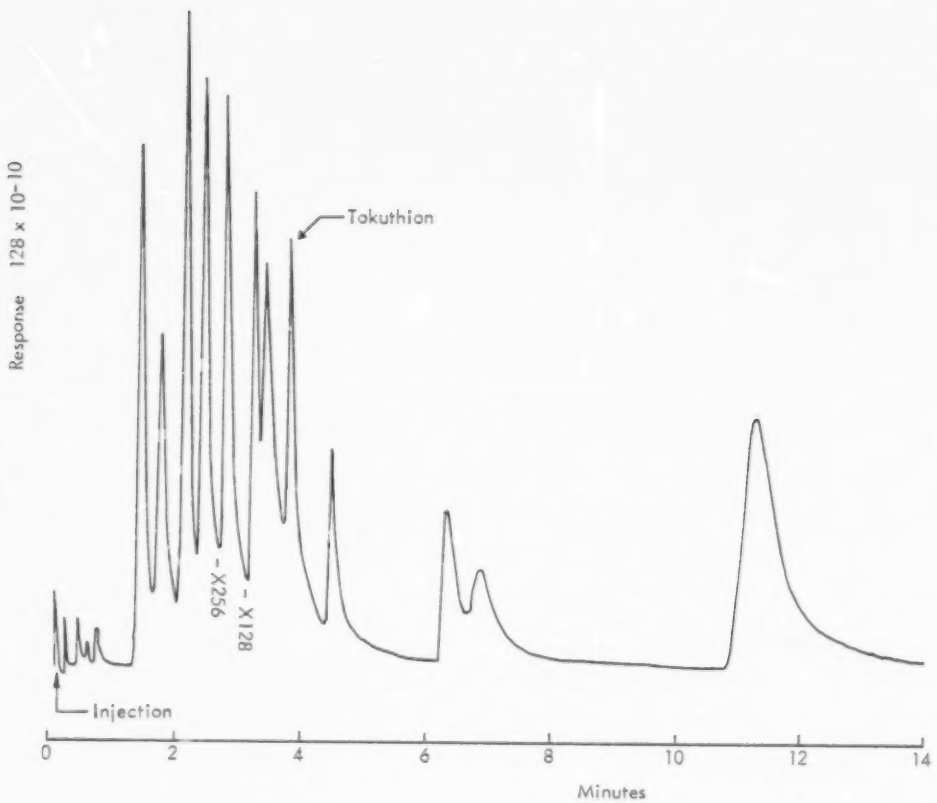


Figure 30. GC/FPD chromatogram of tokuthion in a mixed pesticide standard.

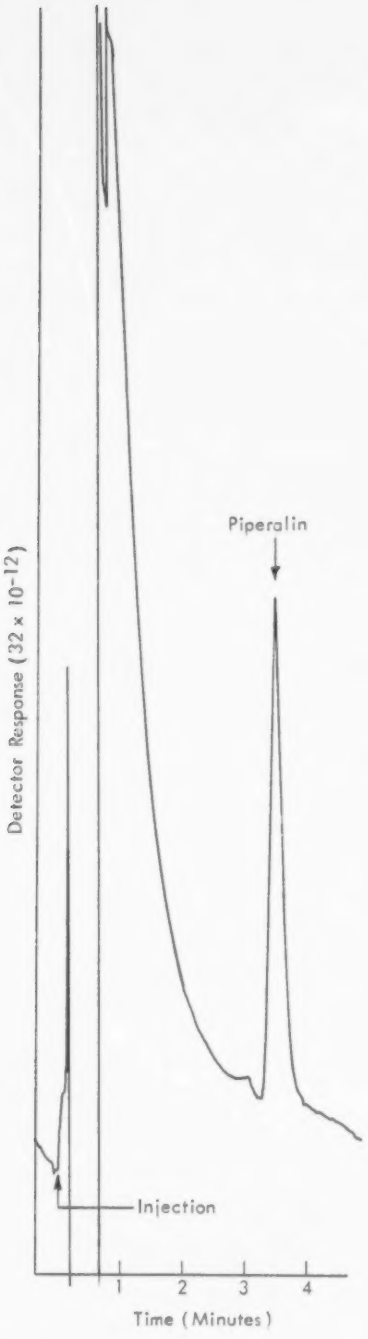


Figure 31. GC/TSD chromatogram of piperalin (8.45 ng).

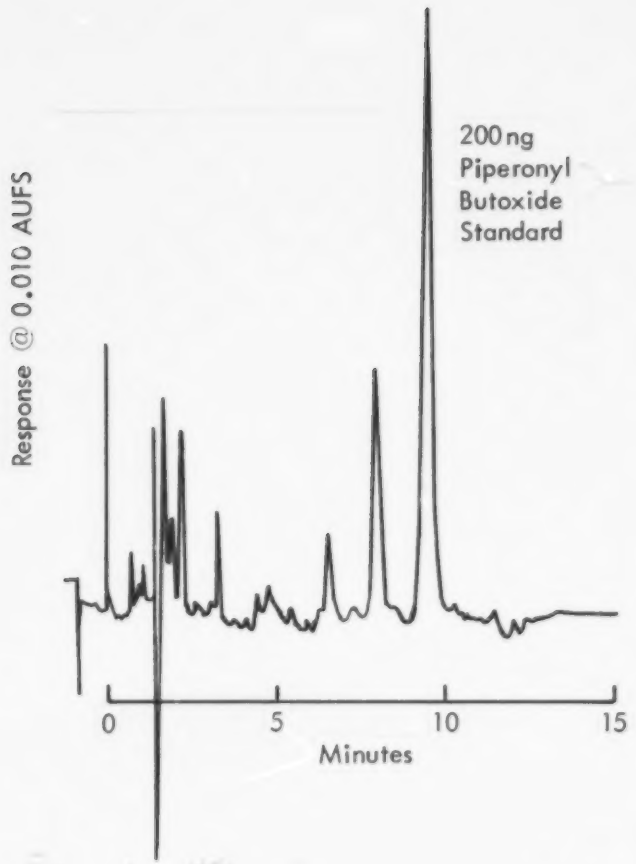


Figure 32. HPLC chromatogram of piperonyl butoxide standard.

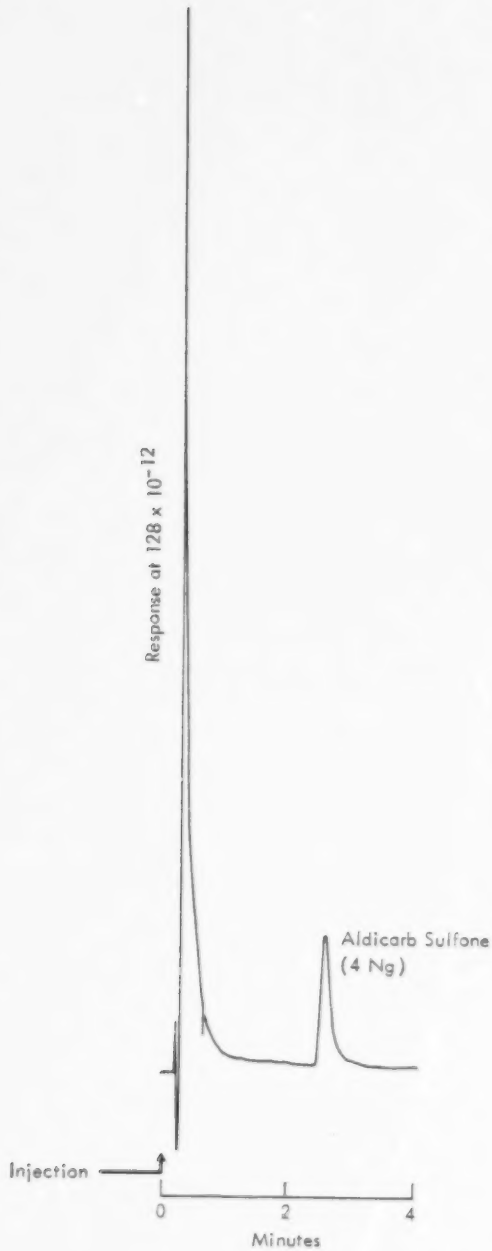


Figure 33. GC/TSD chromatogram of aldicarb sulfone standard (4 ng).

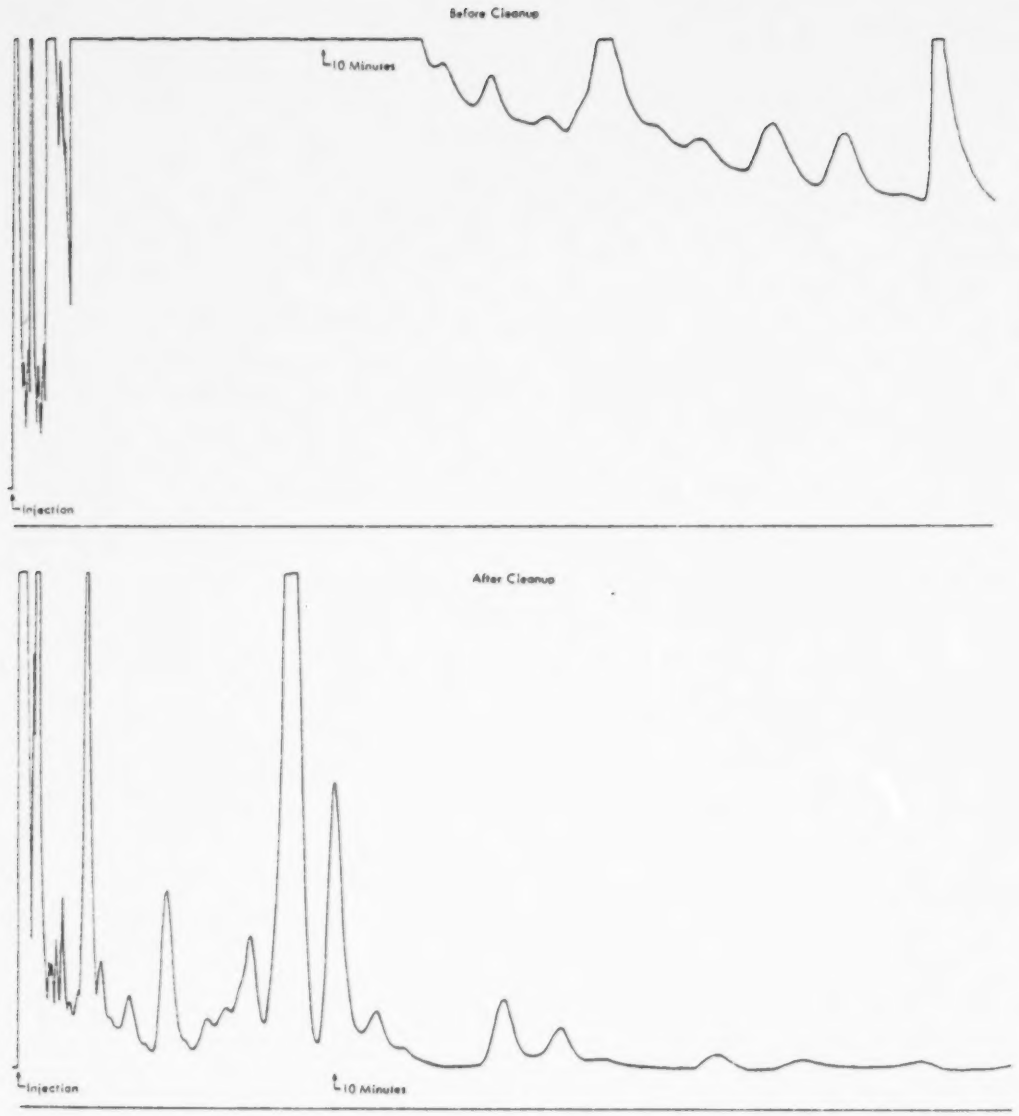


Figure 34. Chromatograms of extract for chloroneb analysis before and after cleanup (manufacturing site C).

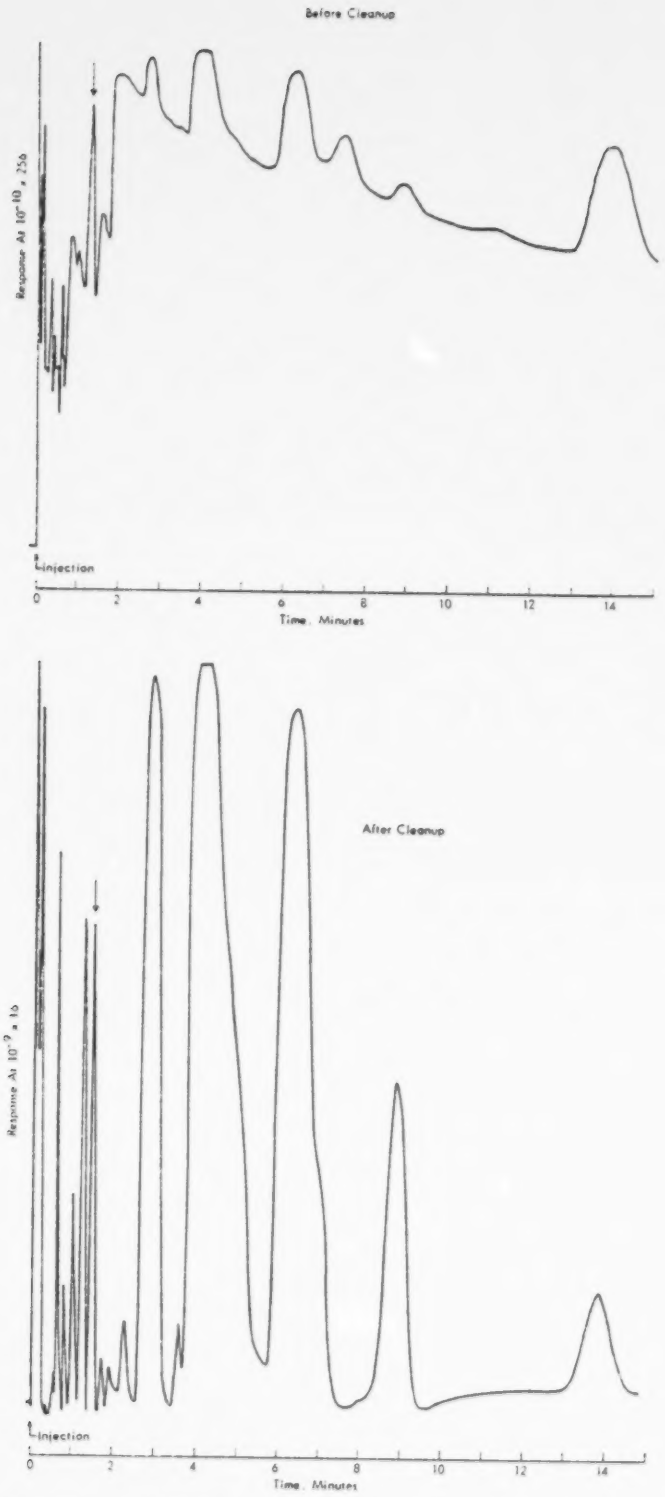


Figure 35. Chromatograms of extract for etridiazole analysis before and after cleanup (manufacturing site E).

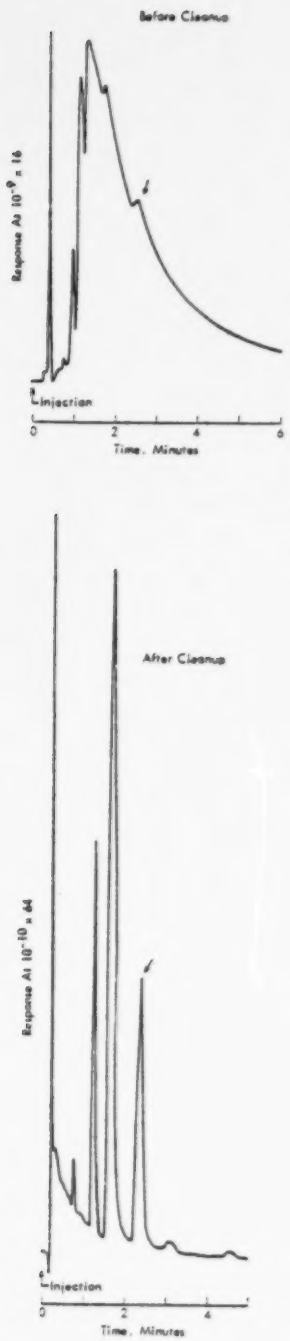


Figure 36. Chromatograms of extract for PCNB analysis before and after cleanup (manufacturing site E).

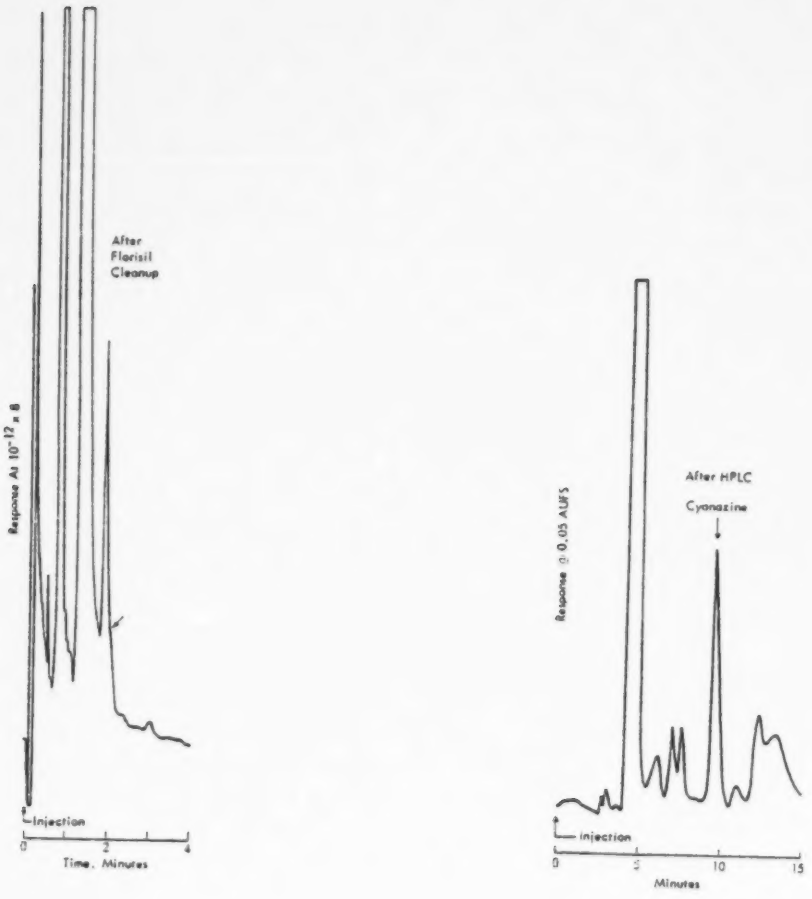


Figure 37. Chromatograms of extract for cyanazine analysis; upper GC/TSD after Florisil cleanup, lower HPLC/UV without cleanup.

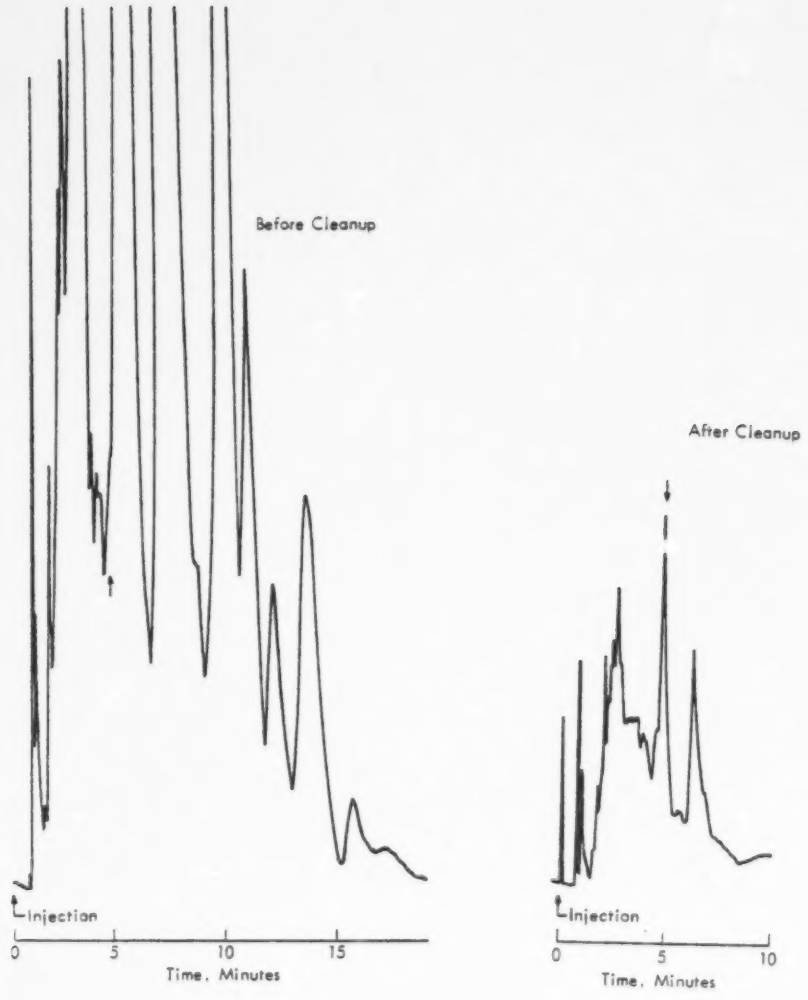


Figure 38. Chromatograms of extract for propachlor analysis before and after cleanup (manufacturing site G).

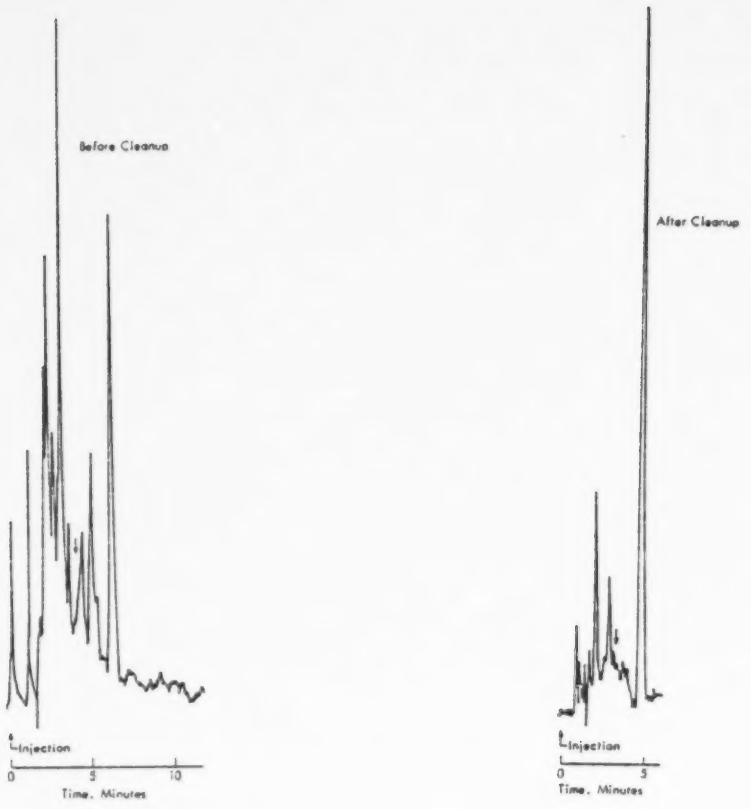


Figure 39. Chromatograms of extract for propoxur analysis before and after cleanup (manufacturing site F).

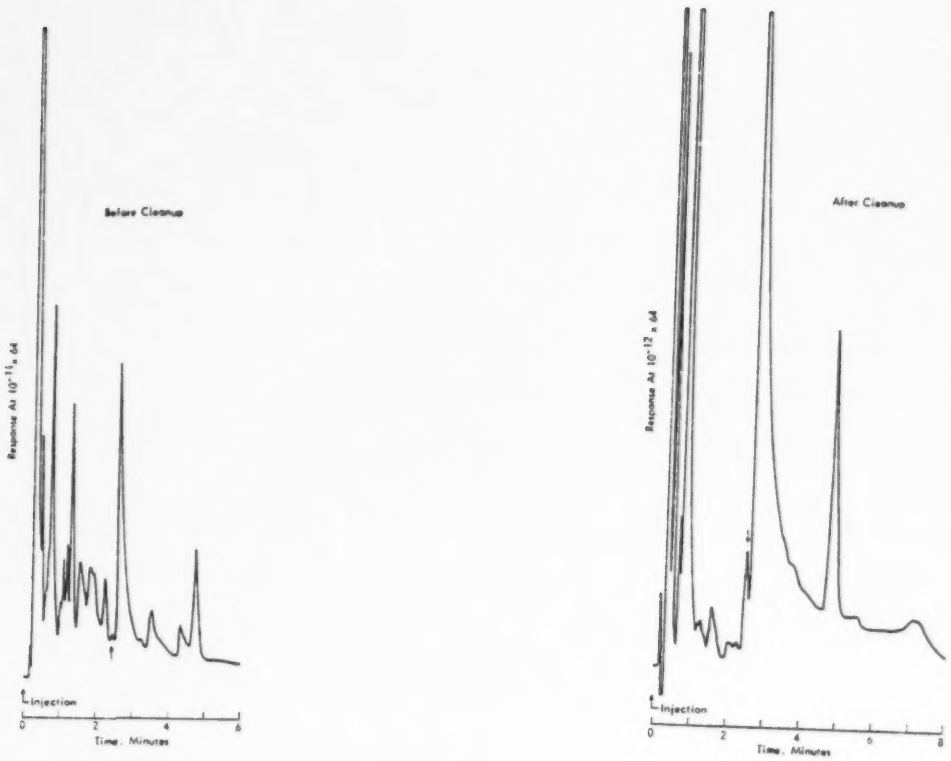
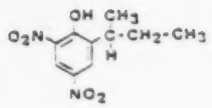


Figure 40. Chromatograms of extract for metribuzine analysis before and after cleanup (manufacturing site F).

APPENDIX

CHEMICAL INFORMATION ON STUDIED COMPOUNDS

Dinoseb

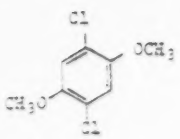


CAS Nomenclature: 2-(Sec-Butyl)-4,6-dinitrophenol

Trade Names: Chemox, Gebutox, Premerge, Knox-Weed, Sinox General, Supersevtox

Molecular Weight: 240

Chloroneb

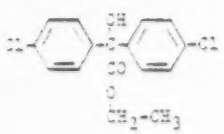


CAS Nomenclature: 1,4-dichloro-2,5-dimethoxy-benzene

Trade Names: Demosan, Tersan

Molecular Weight: 207

Chlorobenzilate

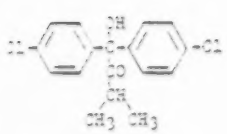


CAS Nomenclature: Ethyl 4,4'-dichlorobenzilate

Trade Names: Acaraben, Acarben, Akar Folbex, G-23992

Molecular Weight: 325

Chloropropylate



CAS Nomenclature: Isopropyl 4,4'-benzilate

Trade Names: Acarilate, Tesakur, Rospin, G-24-163

Molecular Weight: 339

Dibromochloropropane

$CH_2Br-CHBr-CH_2Cl$

CAS Nomenclature: 1,2-Dibromo-3-chloropropane

Trade Names: Nemabrom, DBCP, Fumazone, Nemafame, Nemagon, OS-1897

Molecular Weight: 236

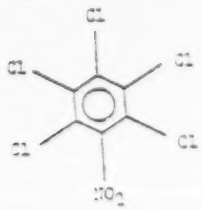
Etridiazole

CAS Nomenclature: 5-ethoxy-3-(trichloromethyl)-1,2,4-thiadiazol

Trade Names: Koban, Terrazole, Truban

Molecular Weight: 247.53

Pentachloronitrobenzene

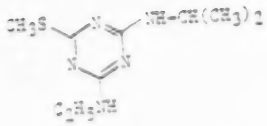


CAS Nomenclature: Pentachloronitrobenzene

Trade Names: Terraclor, Brassicol, Tritisan

Molecular Weight: 295

Ametryn

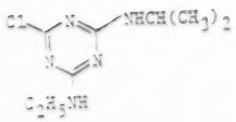


CAS Nomenclature: N-ethyl-N-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine

Trade Names: Gesapax; G-34,162; EVIK

Molecular Weight: 227

Atrazine



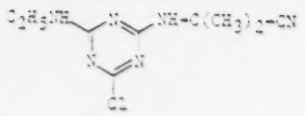
CAS Nomenclature:

6-chloro-N-ethyl-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine

Trade Name: Aatrex®
Atratol®
Gesaprim®
Primatol®

Molecular Weight: 215.5

Cyanazine



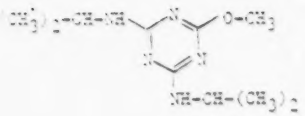
CAS Nomenclature:

2-{[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino}-2-methylpropanenitrile

Trade Name: Bladex®
Fortrol®

Molecular Weight: 240.5

Prometone



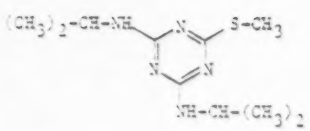
CAS Nomenclature:

6-methoxy-N,N-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine

Trade Name: Pramitol®
Primatol®
Prometon
Prometone

Molecular Weight: 225

Prometryne



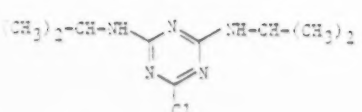
CAS Nomenclature:

N,N-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine

Trade Name: Caparol
G-34161
Gesagard
Prometryn

Molecular Weight: 241

Propazine



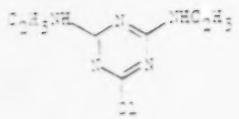
CAS Nomenclature:

6-chloro-N,N-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine

Trade Name: G-30028
Gesamil®
Milogard®

Molecular Weight: 229.5

Simazine



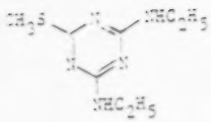
CAS Nomenclature:

6-chloro-N,N-diethyl-1,3,5-triazine-2,4-diamine

Trade Name: CDT
CET
Geigy-27692
Gesatap®
Primatol®
Princep®
Simazin

Molecular Weight: 201.5

Simetryne



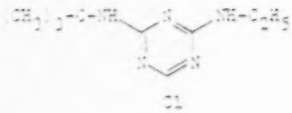
CAS Nomenclature:

N,N-diethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine

Trade Name: G-32911
Simetryn®

Molecular Weight: 213

Terbutylazine



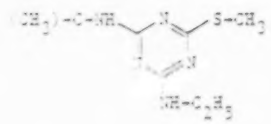
CAS Nomenclature:

6-chloro-N-(1,1-dimethyl-ethyl)-N-ethyl-1,3,5-triazine-2,4-diamine

Trade Name: GS-13529

Molecular Weight: 229.5

Terbutryn



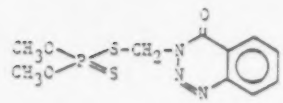
CAS Nomenclature:

N-(1,1-dimethylethyl)-N-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine

Trade Name: GS-14260
Ingran®
Prebane®

Molecular Weight: 241

Azinphosmethyl



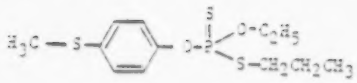
CAS Nomenclature:

O,O-dimethyl phosphorodithio-
-ate S-ester with 3-(mercapto
-methyl)-1,2,3-benzotriazin
-4(3H)-one.

Trade Name: Gusathion®
Guthion®
B-17147
Cotnion-methyl®

Molecular Weight: 317

Bolstar



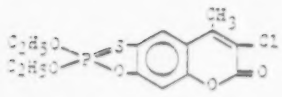
CAS Nomenclature:

[4-(methylthio)phessyl]S-
propyl phosphorodithioate

Trade Name: Bolstar
BAY NTN 9306

Molecular Weight: 322

Coumaphos



CAS Nomenclature:

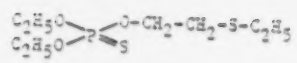
O,O-diethyl O-(3-chloro-4-
methyl-7-coumarinyl)
phosphorothioate;
3-chloro-4-methyl-7-coumarinyl
diethyl phosphorothioate;
3-chloro-7-hydroxy-4-methyl
coumarin O-ester with O,O-
dimethyl phosphorothioate.

Trade Name: Asuntol®
Co-Ral®
Muscatox®
Resitox®
7-Co-ral®
B-21/199

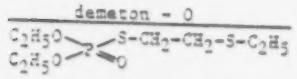
Molecular Weight: 362

Demeton

a mixture of:



demeton - O



demeton - S

Normally contains about:
65% of O-isomer
35% of S-isomer

CAS Nomemclature:

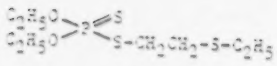
demeton-O: O,O-diethyl O-[2-(ethylthio)ethyl] phosphorothioate

demeton-S: O,O-diethyl S-[2-(ethylthio)ethyl] phosphorothioate

Trade Name: mercaptophos
Systox®
B-8173

Molecular Weight: 258

Disulfoton



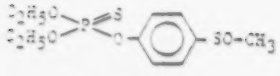
CAS Nomenclature:

O,O-diethyl S-[2-(ethylthio)-ethyl] phosphorothioate; S-(2-ethylthio-ethyl)phosphorothiolothionate.

Trade Name: Di-Syston®
Dithiosystox®
Ekatine® Frumin®
Solvirex®
B-16939

Molecular Weight: 274

Fensulfothion



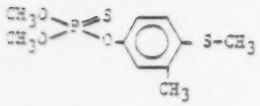
CAS Nomenclature:

O,O-diethyl O-[4-(methylsulfinyl)phenyl]phosphorothioate; diethyl 4-(methylsulfinyl) phenyl phosphorothionate.

Trade Name: Dasanit®
Terracur P®
B-25141
DMSP

Molecular Weight: 308

Fenthion



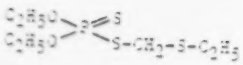
CAS Nomenclature:

O,O-dimethyl O-(3-methyl-4-methylthiophenyl) phosphorothioate;
O,O-dimethyl O-[4-(methylthio)-m-tolyl]phosphorothioate.

Trade Name: Baycid®
Baytex®
Entex®
Figuron®
Labaycid®
Queletox®
Spotton®
Tiguvon®

Molecular Weight: 278

Phorate



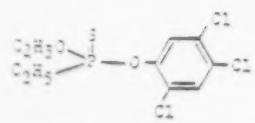
CAS Nomenclature:

O,O-diethyl S-[(ethylthio)-methyl]phosphorodithioate;
diethyl-S-(ethylthiomethyl)-phosphorothiolothionate.

Trade Name: Thimet®
Granutox®

Molecular Weight: 260

Trichloronate



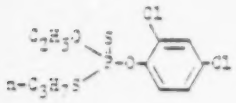
CAS Nomenclature:

O-Ethyl 2,4,5-trichlorophenyl-ethylphosphonothioate

Trade Name: Agritox
Phytosol
Bayer 37 289
54400

Molecular Weight: 333.6

Tokuthion

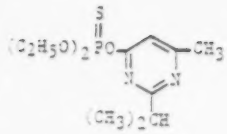


CAS Nomenclature:
O-Ethyl-O-(2,4-dichlorophenyl)-S-propylphosphorodithioate

Trade Name: Tokuthion
Bay NTN 9629

Molecular Weight: 344

Diazinon

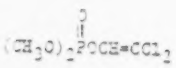


CAS Nomenclature: O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorothioate

Trade Names: Basudin, Neocidol Nucidol, Spectracide

Molecular Weight: 304

Dichlorvos

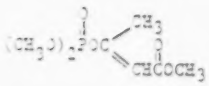


CAS Nomenclature: 2,2-dichloroethenyl dimethyl phosphate

Trade Names: Herkol, Nogos, Nuvan Phosuit, Vapona

Molecular Weight: 220.98

Mevinphos

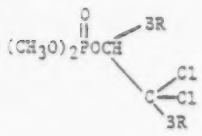


CAS Nomenclature: Methyl 3[(dimethyloxyphosphinyl)oxy]-2-butenoate

Trade Name: Phosdrin

Molecular Weight: 224

Naled

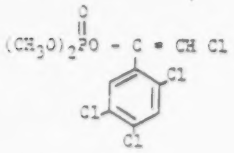


CAS Nomenclature: 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate

Trade Name: Dibrom

Molecular Weight: 380.80

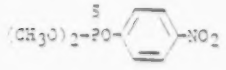
Stirofos (tetrachlorvinphos)



CAS Nomenclature: (Z)-2-chloro-1-(2,4,5-trichlorophenyl)ethenyl dimethyl phosphate

Trade Names: Gardona, Rabon

Methyl Parathion

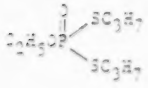


CAS Nomenclature: O,O-Dimethyl-O-(4-nitrophenyl) phosphorothioate

Trade Names: Dalf, Folidol-M, Metacida, Nitrox 80

Molecular Weight: 263

Ethoprop

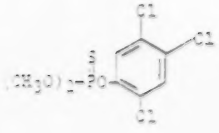


CAS Nomenclature: O-ethyl S,S-dipropylphosphorodithioate

Trade Names: Mocap, Prophos

Molecular Weight: 242

Ronnel

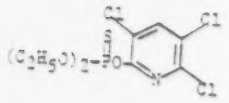


CAS Nomenclature: O,O-Dimethyl-O-(2,4,5-trichlorophenyl) phosphorothioate

Trade Names: Korlan, Nowkor, Trolene

Molecular Weight: 321

Chlorpyrifos

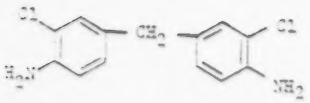


CAS Nomenclature: O,O-Dimethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorochioate

Trade Names: Dursban, Lorsban

Molecular Weight: 350

MOCA

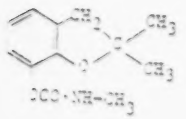


CAS Nomenclature: 4,4'-methylene bis(2-chloroaniline)

Trade Names: Curene 442

Molecular Weight: 266

Carbofuran

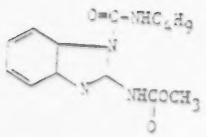


CAS Nomenclature: 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate

Trade Name: Furadan

Molecular Weight: 221.3

Benomyl

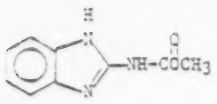


CAS Nomenclature: Methyl[1-[(butyl-amino)carbonyl]-1H-benzimidazol-2-yl]carbamate

Trade Names: Benlate, Tersan

Molecular Weight: 290

Carbendazim

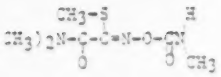


CAS Nomenclature: Methyl 1-H-benzimidazol-aylcarbamate

Trade Names: Banistin Derosal

Molecular Weight: 191

Oxamyl

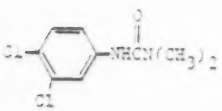


CAS Nomenclature: Methyl 2-(dimethylamino)-N-[[(methyl amino)-carbonyl]oxy]-2-oxoethanimidothioata

Trade Name: Vydate

Molecular Weight: 219.3

Diuron

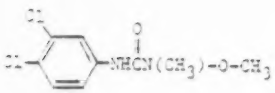


CAS Nomenclature:

3-(3,4-dichlorophenyl)-1,1-dimethylurea

Molecular Weight: 233.1

Linuron

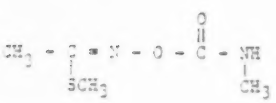


CAS Nomenclature:

N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea

Molecular Weight: 249.1

Methomyl



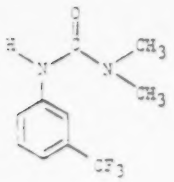
CAS Nomenclature:

Methyl N-[[(methylamino)carbonyl]-oxy]ethanimidothioata

Trade Names: Lannate

Molecular Weight: 162.2

Fluometuron



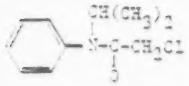
CAS Nomenclature: 1,1-Dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea

CAS No.: 2164-17-2

Trade Names: Cotoran, CIBA-2059

Molecular Weight: 232

Propachlor

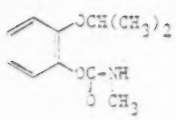


CAS Nomenclature: 2'-chloro-N-isopropylacetanilide

Trade Names: Ramrod

Molecular Weight: 211.7

Propoxur

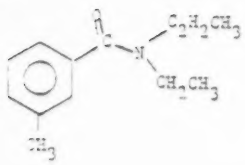


CAS Nomenclature: 2-(1-methylethoxy)-phenyl methyl carbamate

Trade Names: Baygon, Blattanex, Unden

Molecular Weight: 209

Deet

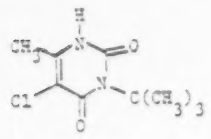


CAS Nomenclature: N,N-Diethyl-3-methyl-benzamide

Trade Names: Deet, Delphene, Metadelphene

Molecular Weight: 191.3

Terbacil

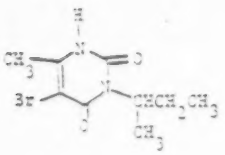


CAS Nomenclature: 5-Chloro-3-(1,1-dimethylethyl)-6-methyl-2,4(1H,3H)-pyrimidinedione

Trade Name: Sinbar

Molecular Weight: 216.7

Bromacil

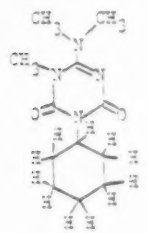


CAS Nomenclature: 3-Bromo-6-methyl-3-(1-methylpropyl)-2,4(1H,3H)-pyrimidinedione

Trade Name: Hyvar

Molecular Weight: 261.1

Hexazinone

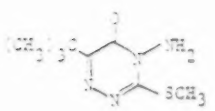


CAS Nomenclature: 3-Cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione

Trade Name: Velpar

Molecular Weight: 252.3

Metribuzin

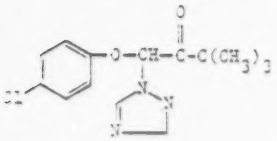


CAS Nomenclature: 4-Amino-6-tert-butyl-3-(methythio)-as-triazin-5(4H)-one

Trade Names: Sencor, Senconal

Molecular Weight: 214.3

Triadmefon

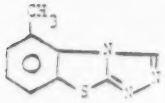


CAS Nomenclature: 1-(4-Chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazo-1-yl)-2-butanone

Trade Name: Bayleton

Molecular Weight: 293.5

Tricyclazole

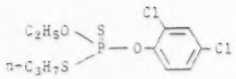


CAS Nomenclature: 5-Methyl-1,2,4-triazolo-[3,4-b]benzothiazole

Trade Name: Tricyclazole

Molecular Weight: 189.2

Tokuthion

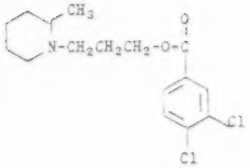


CAS Nomenclature: O-ethyl-O-(2,4-dichlorophenyl)-S-propylphosphoro-dithioate

Trade Names: Tokuthion; BAY NTN 8629

Molecular Weight: 344

Piperalin

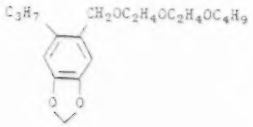


CAS Nomenclature: 3-(2-Methylpiperidino)propyl-3,4-dichlorobenzoate

Trade Names: Pipron

Molecular Weight: 330

Piperonyl Butoxide

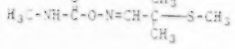


CAS Nomenclature: 5-[[2-(2-butoxyethoxy)ethoxy]methyl]-6-propyl-1,3-benzodioxole

Trade Names: Butocide

Molecular Weight: 338

Aldicarb



CAS Nomenclature: 0-[(methylamino)-(carbonyl)]oxime

Trade Names: Temik

Molecular Weight: 190.3